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SCIENTIFIC MEMOIRS,

SELECTED FROM

THE TRANSACTIONS OF

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AND LEARNED SOCIETIES,

AND FROM

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EDITED BY

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"Every translator ought to regard himself as a broker in the great intellectual traffic of the world, and to consider it his business to promote the barter of the produce of mind. For, whatever people may say of the inadequacy of translation, it is, and must ever be, one of the most important and meritorious occupations in the great commerce of the human race."—Goethe, *Kunst und Alterthum*.

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PREFACE TO THE FOURTH VOLUME.

ON the publication of the Sixteenth Part of the Scientific Memoirs, completing the Fourth Volume, I may remark, as the progress of the work has been slower than before, that I have of late been left to my own means for its continuation, as since 1841 it has no longer received support from the British Association. I trust, however, that although the Parts have appeared at longer intervals, their contents will be found quite equal in interest and importance to those of the preceding volumes.

Keeping in view the object of the work, as designed to assist in elucidating the subjects of inquiry which from time to time engage the attention of men of science in our own country, the present Volume includes a series of Memoirs on the Heat and Elasticity of Gases and Vapours, by Holtzmann, Magnus, and Regnault; whilst on subjects connected with the Theory of Light and Colours, will be found those of Wartmann, Neumann, Seebeck, and especially that of Biot on Polarized Light, which of itself is a work of considerable extent.

For the Memoirs of MM. Plateau, Wartmann and Dove, I am indebted to the authors, who kindly communicated them to me. I have also to acknowledge the valuable assistance which I have received during the progress of the Volume from Professors Faraday, Challis, Graham, Lloyd, W. H. Miller, Wheat-

stone and E. Forbes; also from Sir David Brewster, Sir John Lubbock, Sir John Richardson, James Dixon, Esq., J. J. Bennett, Esq., Col. Sabine, and from Dr. W. Francis, upon whose aid I have principally depended.

The succeeding Part, to commence a Fifth Volume, is already in preparation; and I trust I may be enabled to continue the work acceptably to the public, as valuable materials shall present themselves.

RICHARD TAYLOR.

London, Dec. 24, 1846.

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SCIENTIFIC MEMOIRS.

VOL. IV.—PART XIII.

ARTICLE I.

On the Chemical Reactions produced by Bodies which act only by Contact. *By Prof.* M. E. MITSCHERLICH.

[From the *Annales de Chimie et de Physique*, Janv. 1843.]

FOR however long a time we leave a mixture of hydrogen and oxygen, these gases never combine, even in the presence of such bodies as sulphuric acid, potash or lime, which have a great affinity for water, and which apparently should stimulate its formation. When, however, metallic platinum is introduced into a mixture of these gases, their combination is effected instantaneously on the metallic surface.

The mixture of these gases may be made in the proportions to form water, and at the end of a very short time the hydrogen and oxygen are so intimately mixed that each molecule of the one must be in the presence of a molecule of the other; since the molecules of gaseous bodies possess an exceeding great mobility, and their cohesion is no obstacle to their combination, as is the case with solid and liquid bodies; and since the affinity of hydrogen and of oxygen in water may be supposed to be equal to a pressure of several millions of atmospheres; it must surely, then, be admitted, that besides the ordinary reasons that are opposed to the chemical combination, there is some other which prevents the combination of hydrogen and oxygen by neutralizing their natural affinity.

Some bodies in solution behave to each other in the same manner as hydrogen and oxygen do with regard to platinum. A solution of cane sugar may be left for a very long time without its undergoing any change; but if dilute sulphuric acid be added

to it, the sugar, without combining with the sulphuric acid, fixes some water and is converted into glucose. The decomposition of ammoniacal gas by incandescent copper is one of the few examples in which decomposition of a gaseous body is induced by a solid body; but there are on the other hand numerous examples of this class of decompositions between liquid and solid bodies which themselves undergo no change in the reaction; such for instance are the decomposition of the peroxide of hydrogen by various bodies, the decomposition of chlorate of potash by the oxide of copper and other fixt bases.

Before it is possible to ascertain why certain chemical reactions are effected under the influence of bodies which act only by their presence, we should seek to form a clear notion of the manner in which bodies that do not combine chemically behave when brought into close contact. The attraction which a solid exercises on a gaseous body may be shown with the greatest facility, by employing the former in such a state that it offers the greatest possible surface in the smallest volume, in extremely thin leaves, or, better still, in impalpable powder. Carbon and several other substances scarcely fusible, such as platinum, which may be obtained in a state of extreme division, are well suited for such inquiries.

In the first volume of my 'Manual of Chemistry,' I have calculated the surface which would be represented by a cubic inch divided into small cubes of $\frac{1}{2400}$th of an inch laterally by two series of perpendicular sections. It equals, neglecting the size of the cells, 100 square feet. If any substance be prepared in such a state of fineness that its division may be supposed to have stopt short only at its atom, or at least at a degree the approximation of which is known, the surface which it would represent might still be calculated. Mathematics can furnish the value of the greatest diameter of an atom of a chemical compound, when this can be obtained in the state of thin laminæ or of vesicles; thus the diameter of an atom of water must be at the furthest $\frac{1}{10.000.000}$th of an inch, from the colour which the thinnest film of a soap bubble presents.

By reducing a dilute solution of chloride of platinum by means of carbonate of soda and formic or tartaric acid, or by decomposing a very weak solution of the sulphate of platinum by weak alcohol, the metallic platinum obtained in both cases must be in the molecular state, since the molecules at the moment of the

reduction are separated by the water which necessarily prevents their agglomeration. A volume of one cube inch filled with globules, which we will suppose for greater facility not to exceed $\frac{1}{10,000,000}$th of an inch in diameter, but arranged so that lines passing through their centres are mutually perpendicular or parallel, will present a surface of 218,166 square feet. In every other position the surface would still be increased if they touched; it is possible that platinum black offers a surface of this extent.

Charcoal is best adapted for investigating the action of large surfaces on gases, and the experiments of Saussure on this subject are of the greatest importance. Vegetable fibre does not fuse when ignited with care, so that the charcoal resulting from its calcination still preserves the form of the fibre; this is very evident, for when a carbonized section of wood is placed under the microscope, the walls of the cells are found to have remained intact.

The cells of charred wood are on an average $\frac{1}{2400}$th of an inch in diameter; their surface would therefore be equal to 100 square feet, supposing the charcoal itself to occupy no space. I prepared a piece of charcoal, which weighed 0·9565 grm., by boiling it for some time with pure water, and then simply wiping its surface; it now weighed 2·2585 grms., and under water 0·110 grm. The space which the water had occupied, and which consequently elastic fluids might enter in their turn on the expulsion of the water, would amount then to five-eighths of the entire volume of the charcoal; taking into account the space occupied by the charcoal itself in order to calculate the extent of the surface, this does not amount to more than 73 square feet. Saussure found that charcoal absorbed thirty-five times its volume of carbonic acid at 12° C. and at a pressure of 26·895; but these 35 volumes of carbonic acid are contained in the space which forms five-eighths of the total volume of the charcoal, and consequently fifty-six times less than the space originally occupied by the carbonic acid.

According to the experiments of M. Addami, carbonic acid becomes liquid at a pressure of 36·7 atmospheres, the temperature being 12° C.; we are therefore led to conclude that more than one-third of the carbonic acid condensed in the pores of the charcoal is in a liquid state on the walls of the cells.

If 35 square inches of carbonic acid are condensed on a sur-

face of 73 square feet, or of 10,512 square inches, the thickness of the layer of carbonic acid clothing the walls of the cells must be represented by 0·000002 inch. This layer is more dense when the experiment is made with ammoniacal gas, hydrochloric acid, or sulphurous acid, which do not require such enormous pressure to become liquid, and which are absorbed in far greater quantity. Since all porous bodies which offer a considerable surface to the gas act in the same manner as charcoal, it necessarily follows that the gases in contact with solid bodies must be in a particular state, such as they do not present when removed from them; and moreover, since the thickness of the layer of condensed gas varies, the attraction is not manifested solely on the gas which is in immediate contact with the solid body; it acts at variable distances. But porous bodies do not act solely by their surface; for if this were the case, the absorption of different gases by different substances ought to take place in the same ratio. Such is not the case, for, according to M. de Saussure, wood condenses proportionally more carbonic acid than charcoal; in the same way, asbestos, meerschaum, cotton and silk tissue, absorb the various gases in other proportions than box-wood charcoal.

The absorbing power of pulverulent substances has up to the present time been very little studied; platinum black, prepared by Davy's method, greatly surpasses all others; 10 grains condense 0·550 cube inch of oxygen, that is to say, one cube inch would condense 253,440 cube inches (*Chimie du Platine*, by Döbereiner, p. 64); but it is impossible to decide what is the volume which the platinum occupies when it has condensed oxygen, because it is in a state of powder. The property which some bodies, such as silica, possess of condensing the humidity of the air, may authorize our concluding that they are adapted for condensing gases.

In the same manner that solid bodies attract gases, so are they also capable of exercising this attraction upon liquid bodies or other solid bodies; thus we may, by means of box-wood charcoal, separate from alcohol the potatoe oil which it holds in solution; on boiling the charcoal with water, the oil passes off unaltered in company with the latter: this force of attraction takes up solid colouring matters from liquids which hold them in solution.

Some precipitates have the property of carrying down a part

of the soluble salts which surround them; but they may be finally removed by edulcoration.

I dissolved some nitrate of barytes in ten parts of water; after having precipitated nearly the half of this by sulphuric acid, when the precipitate was settled, I determined the quantity of nitrate of barytes which the clear liquid above the precipitate contained. The filtrated liquid coming from the washing of the precipitate was evaporated, and the quantity of nitrate of barytes which it contained ascertained. By subtracting the weight of this nitrate and the weight of the sulphate of barytes obtained from the total weight of the moist precipitate, the weight of the water contained in the liquid was ascertained. Calculating according to these data, on the one hand the weight of the nitrate of barytes contained in the liquid supernatant upon the sulphate formed, and on the other hand that of the liquid which moistened the precipitate, we find that two-thirds only of this last were dissolved, and that the remaining one-third, which is found in the water employed for edulcoration, must be condensed by the attraction exercised by the precipitated sulphate. If, instead of precipitating a solution of nitrate of barytes, chloride of barium be employed, none of this latter is carried down. But if a solution of nitrate and of sulphate of soda be precipitated by the nitrate of barytes, and the precipitate be washed until a drop of the water no longer leaves any trace of solid matter upon evaporation on platina foil, the sulphate of barytes in this case is able to retain 2 per cent. of nitrate of soda; in order to remove which the precipitate must be calcined and afterwards washed.

The sulphate of barytes thus exercises so feeble an attraction on the chloride of barium, that it cannot abstract it from its aqueous solution; with respect to the nitrate, the attraction is already sufficiently strong to render a large quantity of water necessary to remove it; but the water is incapable of completely removing from the sulphate of barytes the nitrate of soda which it takes up when in the act of forming.

We may very well estimate the force of attraction which solid bodies mutually exert on one another, by considering the action of strong glue on wood and glass; if a plate of glass be covered with a moist bladder, and after drying it we attempt to detach it, we remove morsels of glass. The attraction exercised by the bladder upon the glass is therefore stronger than the cohesion of the molecules of the glass itself; but if the plate of glass

covered with the dry bladder be left for some time in boiling water, the gelatine dissolves, and it may be removed with ease.

Although this attraction is very strong, it is however less considerable than that of the sulphate of barytes for the nitrate of soda. The attraction exercised by solids upon liquid and gaseous bodies, is not only manifested by immediate contact, but also at a determinable distance. This may be proved by employing thin plates of glass or quartz having completely smooth surfaces. The first is suspended, and the second furnished with an apparatus in which weights may be placed. From two plates thus arranged I removed all adherent moisture; the thinnest layer interposed would have been recognised by means of the coloured rings of Newton; on subsequently compressing these plates until the coloured rings begin to appear, it is easy to determine their distance. On the appearance of the second ring, the lower plate, the weight of which was fourteen grammes, remained attached to the first: the approached surfaces were only an inch square; when they were brought near so as to obtain the black of the first ring upon nearly the entire surface, several pounds might be suspended. On leaving this apparatus for some time under the receiver of an air pump, the plates did not detach themselves; atmospheric pressure does not therefore intervene to maintain them in contact.

We know that this kind of attraction is chiefly exerted during the crystallization of bodies. A body dissolved is deposited upon threads or any solid bodies suspended in the liquid, much more speedily than if these were not there. Crystals are deposited much more speedily still around a crystal already formed than in any other portion of the liquid, when, for example, the power of the solvent is diminished by a lowering of the temperature.

The solvent power of the water acts, then, with less energy near a formed crystal than at some distance from it.

In some cases it is very easy to account for chemical combinations which the action of solid bodies on liquids and gases may induce, but in other cases the explanation may be more difficult. It is possible that condensation may be the sole cause with respect to gaseous bodies. In this manner the detonation which M. Thénard observed, on introducing charcoal into a mixture of hydrosulphuric acid and oxygen, may very well be explained; when platinum black, on which oxygen has been condensed, is placed in contact with hydrochloric acid, chlorides of platinum

are formed, according to M. Döbereiner. It is readily intelligible that, in this case, the condensed oxygen can easily combine with the hydrogen of the acid; nevertheless the affinity of the chlorine for the platinum necessarily intervenes also in this action. The affinity of gold for chlorine causes the decomposition of nitric acid by hydrochloric acid when gold-leaf is placed in nitro-muriatic acid, for this does not contain free chlorine until after being warmed, or left to itself for a long time.

When a gas is in *statu nascenti*, a phænomenon analogous to those of which we have just spoken is presented: the gas often combines with a body, which, placed in contact with it, in other circumstances, would not be acted upon by it at all; thus, in cases where the chemical affinity of two gases is feeble, their condensation may cause them to enter into chemical combination.

It however appears doubtful whether the combination of two bodies which, like hydrogen and oxygen, have so great a mutual affinity, should be attributed to the effects of condensation only; although we are justified in admitting that, in the different physical states of platinum, a condensation of gas always takes place on its surface.

We know that platinum acts just as well in thin plates or wire as in the spongy or pulverulent state; but the combinations take place with a slowness proportioned to the smallness of the surfaces employed.

The laminæ and sponge of platinum do not condense a very large quantity of oxygen; but on comparing their surface with that of the platinum black, we perceive that it must be so. The platinum black arising from the decomposition of the double chloride of platinum and potassium is formed at a temperature at which the mixture begins to agglomerate, and it assumes the form of lamellæ, which certainly cannot present a surface considerable enough to permit us to appreciate easily a condensation of gases.

An experiment, which was first made by M. Fusinieri, and which is very easy to repeat, proves that there are air and moisture condensed on the surface of glass. If some boiled mercury, which has been left to cool *in vacuo*, be poured into a glass tube, we notice that it yields air when it is warmed, even when the precaution has been taken to assure ourselves by the microscope that there remained not a trace of it adhering to the sides. But if into a glass tube, which has been exposed to a high tem-

perature, we pour some mercury by means of a funnel the point of which touches the bottom of the tube, and we then heat it, it does not yield the least bubble of air, even if mercury has been used which has been shaken with air and water, and it has been left to dry simply in the open air; thus the gaseous bubbles which the mercury yielded in the first experiment must have come from the air and water condensed upon the sides of the tube; but this quantity of air and water condensed in the first case is so very small, that its presence can only be shown by the experiment which we have just related.

It would be impossible to prove the condensation of any gas on the surface of laminæ of platinum, supposing even that it was as considerable as that of carbonic acid on the surface of charcoal.

A mixture of alcohol and oxygen behave, in presence of platinum, precisely in the same manner as a mixture of hydrogen and oxygen. The oxygen is without action upon the alcohol, weak or concentrated; the platinum black induces their combination. Other bodies are similarly circumstanced. It has been thought that, in order to effect this reaction, it was necessary to have recourse to the employment of ferments, until M. Duflos had proved that shavings of wood steeped in acetic acid acted in an analogous manner to platinum black. It might have been thought that the acetic acid which was employed had deposited ferment upon the shavings; but the ferment would soon have been decomposed by the oxygen of the air; and M. Duflos has proved that alcohol might be converted during entire months into acetic acid with shavings alone.

When acetic acid is prepared by exposing beer or fermented liquors of this kind to the action of the air, they become thick and deposit matters of organic nature. These spongy matters, acting in the manner of platinum black, are able to condense oxygen, and then determine the combination of the bodies.

We can better account for the action of bodies which act by contact, when we study the cases in which they induce decompositions. If we pass some ammoniacal gas over incandescent copper or iron shavings, it is entirely decomposed into nitrogen gas and hydrogen gas; whereas, on passing it over platinum turnings or fragments of glass, only an extremely small quantity on the contrary is decomposed.

The decomposition of the binoxide of hydrogen is of the great-

est importance; it takes place only at the surface of solid bodies, and indeed in the ratio of the extent of that surface; but bases and acids act upon it in quite a different manner; the former excite the decomposition of the binoxide of hydrogen, the latter render it more stable.

The decomposition of the chlorate of potass in contact with oxide of copper, binoxide of manganese, and other oxides of this kind, are likewise peculiarly interesting. When chlorate of potass is heated it melts, and, at a little higher temperature, it is converted into oxygen, chloride of potassium, and into hyperchlorate of potass, which in turn is decomposed into oxygen and into chloride of potassium. But if, instead of heating the chlorate of potass alone, it is previously mixed with one of the oxides which I have just mentioned, it is converted into oxygen and chloride of potassium, at the temperature of its fusion, without the production of hyperchlorate of potass.

To obtain an exact idea of the action of the oxides in these cases, we may make the following experiment. We put into one closed tube a mixture of oxide of copper and chlorate of potass, and into a second introduce only some chlorate; these are furnished with bent tubes for collecting the gases, and are placed together in a metallic bath. At a certain temperature the chlorate mixed with oxide of copper is completely decomposed, whilst the chlorate alone does not yield a trace of oxygen. On mixing the chlorate of potass with silex it behaves exactly as the chlorate alone.

The decomposition of the chlorate of potass is accompanied by a development of heat. This phænomenon occurs during the decomposition of the binoxide of hydrogen. To this heat, or rather to the cause which developes it, is attributable the simultaneous decomposition of the binoxide of hydrogen and of the oxide of silver, as well as of other oxides which part with their oxygen at a high temperature.

The conversion of lignine and of starch into dextrine, that of dextrine, of gum and sugar into glucose, is effected by a liquid body.

It is known that on boiling starch with dilute sulphuric acid, it is speedily converted into dextrine and glucose. At whatever period of the operation we examine the liquid, we always find in it sulphuric acid in a free state and always in the same quantity; but the reaction, which consists of a simple fixation of

water, proceeds with a rapidity proportioned to the greater quantity of sulphuric acid employed.

The same transformation may be effected by using nitric acid, when an intermediate product is obtained, which offers some interest. Forty parts of dry starch are moistened with one and a half part of water, adding to it afterwards 2 per cent. of the weight of the starch of nitric acid; this mixture is then dried, first in the open air, and afterwards in the water-bath. The dry residue dissolves completely in water, and on taking only five parts of water for one part of residue, the solution gelatinizes on cooling. In this state it much resembles the jelly furnished by many mosses, and which is generally prepared from lichens and seaweed. If this solution is boiled for a long time, and especially if a little acid be added to it, it loses the property of gelatinizing. The formation of dextrine and glucose is owing to the fixation of water determined by the action of the acids.

The conversion of starch into dextrine may also be effected by means of a temperature of 150°. Thus acids and heat act in this case precisely as platinum and heat in the combination of hydrogen with oxygen. Diastase, at a temperature of 75°, acts, with respect to the starch, like acids. As no one has hitherto succeeded in obtaining this body in a pure state, it is impossible to prove that it has not undergone some alteration during the conversion of the starch; however, as the reaction is effected by means of so small a quantity of diastase, even impure, we may reasonably admit that it really acts only by contact.

Some hundredths of sulphuric acid, added to a solution of cane sugar, are sufficient, even without the assistance of heat, to convert it into glucose, so that the presence of this body in the liquid may be demonstrated by means of sulphate of copper and potass. Other acids also produce the same change without the application of heat. Acetic acid acts in a similar manner, but requires the assistance of heat.

It is for this reason that lime is added to the saccharine juices of plants from which it is desired to extract cane sugar. I have examined the juice of beetroot, and I have always found it perfectly neutral, so that the transformation of which we have just spoken is impossible in the beetroot itself; but any wound may cause the production of acids, and then the sugar undergoes alterations.

I have obtained the sugar formed by the action of sulphuric

acid upon cane sugar in crystals. The sugar which is procured by adding the yeast of beer to a solution of cane sugar appeared to differ from grape sugar. I have not succeeded in obtaining it crystallized, and it deflects polarized light much less than an equal quantity of grape sugar. Its formation is very remarkable: it is owing to a substance mixed with the globules of ferment; it is the aqueous solution of this matter which determines the conversion of cane sugar into this new sugar. For this reason it is that fermentation takes place much more slowly in a solution of cane sugar, when washed yeast is used instead of common yeast. Common yeast excites fermentation as quickly in a solution of cane sugar as in a solution of glucose.

This kind of sugar differs, moreover, from that which is obtained by melting cane sugar.

By melting cane sugar at a temperature of 106° it becomes completely deliquescent, dissolves in absolute alcohol, ferments when in contact with yeast, and exercises a much smaller influence upon polarized light than grape sugar.

Cane sugar does not crystallize again after having been melted; but if, on the contrary, it is melted with water, taking the precaution not to raise the temperature above 154°, it solidifies on cooling, and a vitreous mass, composed in great part of cane sugar retaining water mechanically inclosed, is obtained. This dissolves the particles of sugar, one after another, and deposits them in the state of crystals; for an amorphous body is more soluble than a crystallized one; the entire mass passes into a crystalline state. It is very easy, by breaking a stick of such sugar, to detect the presence of the water, which is found especially toward the centre and between the crystals. It is possible that the sugar may be identical with that obtained by maintaining for a long time a solution of cane sugar at 110°, and which, according to M. Fensky, exercises no action on polarized light. Perhaps it is also identical with that which M. Péligot and M. Mulder have obtained by boiling cane sugar for a very long time with dilute acids, and which, according to those observers, does not crystallize.

All chemists are agreed with regard to the transformation which glucose and other kinds of sugar undergo during fermentation: it is generally admitted that a third of the carbon of the sugar is converted into carbonic acid, whilst the other two-thirds unite with hydrogen and oxygen to form alcohol; thus, for every

measure of carbonic acid there is formed one measure of alcohol; but, according to the kind of sugar which undergoes fermentation, an elimination or a fixation of water takes place. The first is the case with glucose; the second with the variety of sugar soluble in alcohol. The body which determines this action, the only one by means of which it is capable of being produced, is an organized body.

Without entering into the detail of the opinions to which this phænomenon has given rise, we may discuss the facts, which alone have an interest in this question. Ferment is composed of oval and round globules; these globules are large enough to be retained by filtering paper. If a small quantity of yeast is put into a tube closed at one end by some bibulous paper, and this is then introduced into a solution of sugar, the latter passes through the pores of the paper and undergoes alcoholic fermentation, but only in the tube which contains the yeast. The fermentation takes place in the solution of sugar in which the tube is placed, only after a shorter or longer time, and always under the influence of the globules of yeast, which in the end pass through the pores of the paper, which softens by prolonged contact with the liquid. This experiment proves satisfactorily that the fermentation takes place only at the surface of the globules of yeast.

I have also instituted other experiments, which prove what I have just said. M. Schwann, on his part, has also made some; but they are not so decisive as those which I have just related. I have never observed fermentation without globules of yeast, and the phænomenon is effected always at the surface of the latter.

We require only 1 per cent. of globules of yeast to effect the complete transformation of sugar into alcohol and carbonic acid; and when perfectly organized globules are taken, they undergo scarcely any change during the fermentation; they no longer effect it when they are destroyed. On putting them in contact with bodies which have the property of arresting fermentation, they are seen, when examined with a microscope, to contract at the very instant when these touch them.

Globules of yeast, then, in presence of sugar or of sugar and water, which contain the elements of carbonic acid and alcohol, act precisely as platinum sponge with regard to oxygenated water.

Naturalists who have engaged in the study of the most simple organized bodies, assert that the globules of yeast should be classed

with these; and, in fact, when considering their generation and their development, we cannot draw any other conclusion. They always begin by forming in the fermentable juices of plants before fermentation takes place in them.

It is not till after three days that we remark, in these liquids, microscopic points isolated or united into strings; these points are developed, and it is easily observable that their increase takes place from within outwardly; at last we remark in their interior a granular mass surrounded by a transparent covering. They are often elongated, and they then contain two or three granular particles.

In employing perfect globules of yeast to excite the fermentation of sugar, I have not remarked that they developed themselves; but on leaving the yeast standing for some time, they are seen to ramify in the manner of *Confervæ*. The organized substances which are formed in whey present verticillated ramifications. The deposits which take place in whey at the end of a few days, as well the yeasts, are organized, but they are very often mixed with an unorganized substance. According to the experiments of several naturalists, of MM. Schultz, Schwann and others, these substances are not produced when the access of air is intercepted, or when to the matters susceptible of being converted into ferment, there is only admitted air which has previously been raised to a red heat. This fact would be a proof against *equivocal generation*; whilst, supposing that the origin of an organized body in a liquid proceeds from a point which escapes observation, it would tend, on the contrary, to induce us to admit this mode of generation.

It would be important to know what these bodies would become, if, instead of being developed in the midst of a liquid, their development took place in the open air. Would a fungus be the result, as M. Kützing thinks? A fungoid plant added to a fermentable liquid does not induce fermentation, and humid ferment exposed to the air for a long time is not converted into mould.

The presence of these organized bodies in the intestinal tube of the *Herbivoræ* is particularly interesting: it is easy to be convinced by M. Trommer's test of the presence of grape sugar in an animal which has eaten vegetable matter. It is found in the stomach and in the intestinal canal, as far as the rectum only. We meet with the organized bodies which we are considering in

large quantity in these parts of the organism; but they entirely disappear in the rectum and in the fæcal matter. M. Remack first drew my attention to this subject, and subsequently M. Purkinje, M. Böhn, and my brother have had frequent opportunities of observing them. It is very probable that, besides digestion, a true alcoholic fermentation takes place in the intestinal tube, which occasions flatulencies.

The blood which surrounds the intestinal tube dissolves the carbonic acid which may disengage itself from the lungs without recourse to other channels. These organized bodies, ordinarily of an elliptic form, have two transparent points; sometimes they enclose a granular mass like those of the ferments.

MM. Boutron and Frémy have recently proved that lactine is converted into lactic acid under the influence of caseum, and that this combines with the acid formed. Moreover, on separating the caseum from its combination with the lactic acid, by means of carbonate of soda, a new quantity is produced. The composition of lactic acid is such that it is represented by milk-sugar, less a certain quantity of water. I have repeated these experiments with the same result; but as, in this reaction, a combination of caseum and lactic acid is formed, we must suppose that the affinity of the lactic acid for the caseum intervenes in the phænomenon. Nevertheless the coagulation of milk, in the preparation of cheese, appears owing to other causes, since runnet is commonly employed to effect it.

It is commonly supposed that it is the internal part of the stomach of the calves which determines the coagulation of the milk. It is not so, however: the runnet which I have been able to procure was prepared by means of the mucous and the muscular membranes taken from the stomach, in throwing back the peritoneum; but I have been very well able to coagulate milk by employing other parts of the peritoneum; for example, with the part which covers the cæcum. If the precaution be taken to raise the temperature of the milk a little, the coagulation is produced in a few hours, either by suspending in it the membrane itself, or by pouring into the milk a warm infusion of the latter. The membrane and its infusion have no acid reaction, and the milk remains neutral during its coagulation.

The chemical combinations which are effected by means of substances which only act by contact have much analogy with those which are effected when, for example, a body combines

with a second, and the compound which results enters into combination with a third body.

Sulphurous acid has more affinity for oxygen than the binoxide of nitrogen; however, sulphurous acid does not combine with oxygen when the mixture of these gases is left in contact for a very long time, whereas the binoxide of nitrogen seizes directly on the gaseous oxygen to form hyponitric acid. This yields its oxygen to the sulphurous acid and becomes again binoxide of nitrogen. The oxygen therefore is, in the hyponitric acid, in such a state that it can combine with the sulphurous acid. On placing a mixture of oxygen and sulphurous acid in presence of platina sponge, these two gases combine: the action of the platina is therefore here again the same as in the case of hydrogen and oxygen.

All the processes, and especially the production of the æthers, and of æther itself, lead to the conclusion that chemical decompositions and combinations may be impeded by the respective position of the atoms; but that the force of attraction which certain bodies exercise upon the atoms of those with which they are in contact, may change the position, so as to determine chemical reactions. The manner in which gases behave towards charcoal, and especially towards platinum black, proves that this attraction is very strong, even with regard to bodies of a different nature.

M. Berzelius has given to this force the name of *catalytic force*, with as much reason as the expression 'force of affinity,' &c. has been employed, and understands by this term a force which is peculiar to several bodies which do not intervene chemically in the reactions which they determine, and the activity of which consists in destroying chemical combinations. To connect the name with the phænomena, I have named these substances *contact substances*, and the chemical process, decomposition or combination by contact.

Article II.

On the Phænomena presented by a free Liquid Mass withdrawn from the Action of Gravity. By Professor Plateau, *of the University of Ghent; Member of the Royal Academy of Brussels, &c. &c.**

[From the Memoirs of the Royal Academy of Brussels, vol. xvi. †]

1. Liquids being gifted with an extreme molecular mobility, yield with facility to the action of forces which tend to modify their exterior form. But amongst these forces there is one which predominates so much over the rest, that it almost entirely masks their action: this force is gravity. This it is which causes liquids to assume the form of vessels which contain them; and it is this also which makes smooth and horizontal the portion of their surface which remains free. We can scarcely recognise, along the contour of this free surface, a slight curve which reveals the action of the combined forces of the attraction of the liquid for itself, and of its adherence for the solid matter of the vessel. It is only by observing very small liquid masses, upon which the relative action of gravity is thus weakened, that we can see the influence of other forces upon the figure of these masses manifested in a very forcible manner: thus the small drops of liquid placed upon surfaces which they cannot moisten, assume a spherical form more or less perfect. Leaving these minute quantities, if we wish to observe liquid masses which have freely taken a certain form, we must quit the earth, or rather consider the terrestrial globe itself and the other planets as having been primitively fluid, and having adapted their exterior form to the combined action of gravitation and centrifugal force. Theory then indicates that these masses ought to take the form of spheroids more or less flattened in the direction of their axis of rotation, and observation confirms these deductions of theory. Observation shows us also, around Saturn, a body of annular form, and theory finds, in the combined

* The Editor has to express his obligation to the Rev. Professor Challis, of Cambridge, for his kindness in revising this translation for the press.

† Since the time when this memoir was read (January 15, 1842) the author has revised his manuscript, and made several important modifications, caused, for the most part, by the presentation to the Academy of Sciences at Paris, of a treatise by M. Liouville.

actions of gravity and centrifugal force, means of satisfying the equilibrium of that singular form.

If however we could, by some means, withdraw from the action of gravity one of the liquid masses upon which we have to operate, at the same time leaving it free to be acted upon by other forces which might tend to modify its form, and if our process allowed of giving to this mass sufficiently large dimensions, would it not be very curious to see it take a determinate figure, and to see this figure vary in a thousand ways with the forces on which it depends? Now I have succeeded, by an extremely simple means, in submitting to the above conditions a considerable liquid mass.

2. Fat oils are, it is known, less dense than water and more dense than alcohol. Accordingly we may make a mixture of water and alcohol having a density precisely equal to that of a given oil—of olive oil, for example. Now if any quantity of olive oil is introduced into the mixture thus formed, it is evident that the action of gravity upon this mass of oil will be completely annihilated; for, in virtue of the equality of density, the oil will only hold the place of an equal mass of the ambient liquid. On the other hand the fat oils do not mix with a liquor composed of alcohol and water. The mass of oil must therefore remain suspended and isolated in the midst of the surrounding liquid, and it will be perfectly free to take the exterior form which the forces that may act upon it will give to it.

This being supposed, if the molecular attractions of the oil for itself, those of the alcoholic mixture for itself, and those of this mixture for the oil were identical, there would be no reason that the mass of oil left in the midst of the ambient liquid should take spontaneously one form more than another, since, relatively to all the forces acting upon it, it would be exactly in the same position as an equal mass of alcoholic mixture whose place it would occupy. But it is evident that this identity between the different attractive forces does not exist, and that the attraction of the oil for itself greatly exceeds the two others. The mass of oil therefore ought to obey this excess of its own attractive forces.

We thus come to this conclusion, that our mass of oil may be perfectly assimilated to a liquid mass without weight, suspended freely in space, and submitted to its own proper molecular attractions. Now it is clear that such a mass must take the spherical form.

Well, experiment confirms all this in a complete manner. The mass of oil, whatever its volume, remains in fact suspended in the midst of the alcoholic liquid, and *takes the form of a perfect sphere.*

3. In order to obtain this singular result with facility, it is necessary to take certain precautions, which I will describe.

The first concern the formation of the alcoholic mixture. The density of this mixture necessarily varies with the kind of oil which is used. For the olive oil which I employed, and for the purity of which I cannot vouch, the proper mixture marked 22 degrees on the areometer of Beaumé. If therefore any one wishes to use olive oil, he may always consider the above value as a first approximation, and by successive attempts will bring the liquor at length to the exact point which it ought to reach. To accomplish this, a test tube is filled with the liquor, into which a little oil is afterwards poured by means of a long-necked funnel, which reaches about half way down the test tube. The oil, on reaching the liquor, forms a globule, to which a diameter of about two centimetres must be given, and which a little shake will detach from the mouth of the funnel if it does not detach itself. Then accordingly as this globule falls to the bottom of the liquor, or rises to its surface, we conclude that the quantity of alcohol of the mixture is too great or too small; we therefore add to this a little water or alcohol, taking care to stir it well, and recommence the experiment of the test tube. The same operations are repeated until the globule of oil remains suspended in the liquor, without appearing to have a tendency either to fall or rise. The mixture may then be considered as approaching very nearly the desired point. I say very nearly, for the globule of oil of the test tube being of small dimensions, has more difficulty in moving in the liquor than spheres of a large diameter, and it may seem to be in equilibrium of density with the surrounding liquid, whilst for a larger volume of oil this equilibrium does not exist.

4. When the alcoholic mixture, which I presuppose to be contained in a large glass flask of the ordinary form, has attained this point of approximation, the next thing is to introduce the mass of oil. For this purpose the long-necked funnel which has been mentioned above must be again used, and this must reach to a certain depth in the liquor contained in the flask. Letting the funnel rest on the neck of the latter, we pour the

oil slowly. Then if the alcoholic mixture is by chance exactly in the requisite proportions, the oil forms, at the extremity of the neck of the funnel, a sphere the volume of which increases gradually in proportion as we add this last liquid. When the sphere has attained the volume we desire, the neck of the funnel is withdrawn with caution; the sphere which adheres to it rises with it toward the surface of the liquor, and the oil which it still contains is added to the preceding. Lastly, when the sphere has nearly reached the surface of the alcoholic mixture, a little shake detaches it from the funnel. Ordinarily, however, the mixture has not so exactly the desired density. We then see, in general, several successive spheres of oil formed, which detaching themselves one after another from the mouth of the funnel, fall slowly to the bottom of the flask, or rise to the surface of the alcoholic liquor. In this case all these spheres should in the first place be united into one, which is easily done by the following means. We introduce into one of them the end of an iron wire: the adherence which the oil contracts with this metal then allows the sphere in question to be easily conducted in the ambient liquid, and to be led to join with a second sphere*; by continuing this treatment we soon succeed in uniting all. Then, according as the whole sphere shall remain at the bottom or on the surface of the liquor, add cautiously to the latter a certain quantity of water or of alcohol; and, after having corked the flask, we next turn it several times slowly, and so as not to disunite the sphere of oil, until the mixture is well effected, which will take place when we no longer perceive any striæ in the liquor on looking through it at a window. Lastly, the same operation is to be repeated until the sphere of oil is perfectly in equilibrium in the surrounding liquor.

5. If the experiment has been made, as I have supposed, in a flask of the ordinary form, that is to say cylindrical, the mass of oil does not however appear exactly spherical; it is widened in the horizontal direction; but this is only an optical illusion, attributable to the form of the flask: the latter, with the liquor which it contains, acts in the manner of a cylindrical lens whose

* In order thus to compel two spheres to unite, it does not suffice to put them in contact with one another: they might touch for a long time without mingling into one; one would say that they are enveloped in a resisting pellicule which opposes their union. It is also necessary, therefore, to introduce the extremity of the metallic wire into the second sphere, as if we wished to break the partition which separates the two masses: the union is then effected immediately. I shall revert to these phænomena hereafter.

axis would be vertical, and enlarges in appearance the horizontal dimensions of the object.

In order entirely to avoid this illusion, we must use a vessel of plane smooth sides, formed of plates of glass set in a metal frame (§ 8). We then have, in a complete manner, the curious spectacle of a considerable mass of liquid presenting the form of a perfect sphere, and imitating in some measure a planet suspended in space.

Instead also of the above vessel, a glass balloon may be used, which is more simple and less expensive. In this case, indeed, the mass of oil only appears in its real figure when it occupies the centre of the balloon; but the apparent distortion is small, as long as the sphere does not remove considerably from this centre. A vessel of this kind is very convenient for most of the experiments which I shall describe in this part of the memoir; but it would not serve for those which I shall have to make known subsequently.

6. Now, having obtained, by means of the process above detailed, a fine sphere of oil well suspended, and presenting, I will suppose, a diameter of 6 to 7 centimetres, we shall observe the following circumstances, which it is important to notice before we proceed further.

In the first place, the equilibrium, previously well established, is soon disturbed of itself: at the end of a few minutes we see the sphere quit its place, and rise with extreme slowness towards the upper part of the ambient liquid. If a little alcohol be then added to restore the equilibrium, on treating the mixture by the process of § 4, this equilibrium is again broken in the same manner at the end of a certain time. In fine, it is only by continuing for some days to maintain it by the successive addition of small quantities of alcohol, that we come to obtain a permanent equilibrium, which is then no further disturbed, except by an accidental cause, of which we shall speak in the following paragraph. If the temperature does not fall below 18° centigr., the above phænomena are the only ones observed; but sometimes, if the temperature remains below that limit, and always if it is below 15°, another effect is manifested, namely a diminution in the transparency of the oil.

These phænomena are owing to a gradual chemical action which takes place between the oil and the alcoholic mixture. The first of these would be very inconvenient in most of the ex-

periments; but happily it may be obviated: this can evidently be effected by employing the two liquids only when they have already exerted upon one another all the action of which they are capable. The oil and the alcoholic mixture which I used are now inert with regard to one another, because having been employed a great number of times, they have had time to exercise the whole of their mutual action. Besides, it is easy, in a short time, to bring the two liquids to that state of relative neutrality, by agitating them together in order to divide the oil and thus to accelerate the action, then separating them by a suitable process. This operation requires some precautions, which we shall examine in § 24, in order not to interrupt the course of the memoir by details which are not now indispensable. In all that follows we shall always suppose that two liquids thus prepared are employed.

7. Another cause disturbs the equilibrium between the sphere of oil and the ambient liquid: this is the variations of temperature, which alter the equality of the two densities; and the degree of sensibility of such a system in this respect would hardly be conceived. For example, when the vessel is carried into a room a little warmer or colder than that in which it had been before, the sphere soon falls in the first case and rises in the second. On the mere application of the hands to the outside of the vessel, it will be seen, after a few seconds, that the sphere begins to fall.

We must be continually on our guard against these effects of temperature, otherwise they disturb the experiments. The following is a recent instance which occurred to me. The oil and the alcoholic liquor were inclosed in different flasks, and the latter contained a very slight excess of alcohol. Having by chance carried these two flasks into a room warmer than that in which they had been, I first introduced into the mixture a certain quantity of oil, which, by reason of the slight excess of alcohol, descended slowly to the bottom of the flask. A short time afterwards I poured in another quantity of oil, and I was surprised to see this on the contrary rise towards the upper part of the mixture. The reason of the singular difference was this: the alcoholic mixture inclosed in one of the flasks was very considerable in quantity relatively to the oil which the other contained. Now, at the first moment, the liquids, not having sensibly changed their temperature, maintained between them the

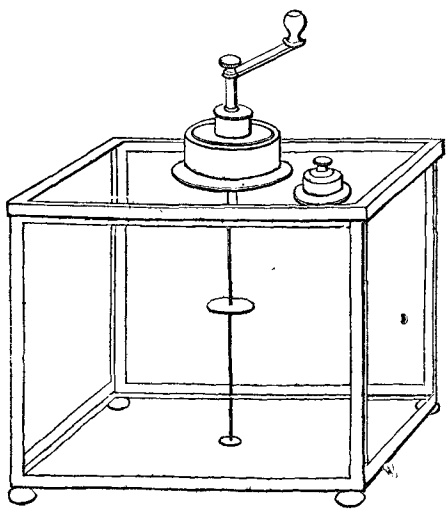
same relation of density; but after a short time the oil, by reason of its small volume, having become warmer than the alcoholic mixture, had thus become relatively lighter. The warmth of the hand which held the flask in pouring out the oil must have also contributed to the effect in question.

8. Now let us suppose a fine sphere of oil in permanent equilibrium in the surrounding liquid, and let us endeavour to submit it to other forces than its own attractions.

The first idea which presents itself is to try the action of centrifugal force. For this purpose it is necessary to impress on the sphere of oil a movement of rotation around one of its diameters, and which is effected by introducing into this sphere a small metallic disc, which is made to turn upon itself by means of an axis which traverses it perpendicularly. This disc carries the oil with it by its adherence, and the whole mass of this liquid takes a movement of rotation.

Before explaining the effects which result from this movement, I shall describe in detail the apparatus I have employed,—an apparatus by the aid of which all the experiments succeeded perfectly and with the greatest facility: it is represented in fig. 1.

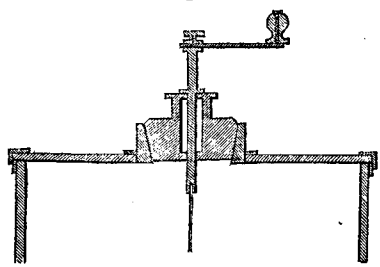
Fig. 1.



The vessel is with plane sides, formed of rectangular plates of glass set in an iron frame; the sides are each 25 centimetres broad and 20 high. The small disc and its axis are also of

iron, a metal whose prolonged contact with oil does not stain it as copper does. The diameter of the disc is about 35 millimetres, and the axis is formed of an iron wire about $1\frac{1}{2}$ millimetre thick. This axis is fixed by its lower end into a hole pierced in the middle of the plate of glass which forms the bottom of the vessel; this hole is closed below by a small plate of iron cemented to the glass. The upper end of the axis is screwed to a larger wire, which forms the prolongation of it, and which, held with a moderate degree of friction [*à frottement doux*], in a piece of which I shall speak hereafter, receives at its other extremity the handle by means of which the disc is turned. When the whole system is in place the disc ought to be half way up the vessel. The square plate of glass which closes the vessel above is pieced with two openings, each furnished with an iron neck, which is closed with a stopper of the same metal. One of these openings is in the middle of the plate, and its diameter is 55 millimetres; it is through the stopper which closes it that the rod passes, *à frottement doux*, which receives on the one side the axis of the disc and on the other the handle. (See fig. 2.) The other open-

Fig. 2.



ing is smaller and is placed near one of the angles of the plate: it serves for introducing into the vessel either the metallic wire by the aid of which we unite the partial masses of oil, or additional portions of alcohol or of mixture at another degree (§ 9), &c., when these operations are to be performed without removing the disc from its place. Lastly, this same plate is cemented into an iron frame, which is turned up all round, so as to fit upon the vessel as a lid upon a box. The upper edges of the vessel have been ground with emery all together after their being placed in the frame, so that the upper plate of glass fits exactly upon them; and by rubbing these edges and the metallic stoppers with a little oil, the vessel, when the plate and stoppers have

been placed, may be considered as perfectly closed and keeping the mixture without evaporation of alcohol.

In my apparatus the plates of glass are fixed to the metallic framing by a resinous cement, and this is slightly attached by the alcoholic mixture. It would perhaps be better to use some glazier's putty; for the alcoholic mixture being prepared so as not to act any more upon the oil (§§ 6 and 24), this latter cement would probably not suffer any alteration. However, the resinous mastic resists to such a degree, that I have been able to leave the alcoholic liquor, without inconvenience, in the vessel for whole months.

The apparatus which I have just described is the best suited for obtaining in all their beauty the phænomena which are the object of these experiments; but, as I have said above, a hollow sphere of glass of pretty large dimensions might be used with less cost and without too much disadvantage, at least for the experiments treated of in this part of the memoir. This ought to be furnished with two tubular openings, one of which would serve for introducing the system of the disc, and the other would effect the same object as the second opening of which we have spoken above.

I shall, however, in what follows suppose all along that the plane-sided vessel above described is the one employed.

9. The apparatus being properly arranged, the next thing is to operate so as to cause a sphere of oil to surround the disc in such a manner that their two centres are sensibly coincident. To attain this point, let us first endeavour, before introducing the disc into the vessel, to bring the centre of the sphere to remain at the height at which that of the disc should be. It would be extremely difficult to accomplish this by suspending a sphere in a homogeneous alcoholic mixture, as we have hitherto supposed: for then there is no reason why the sphere should not stand higher or lower; and if even by chance it were placed exactly at the desired height, the movements which would be produced on introducing the disc would very probably change this height. It is therefore necessary to employ a more sure process, and the following succeeded perfectly:—We begin by causing the alcoholic mixture to contain a small excess of alcohol; then, the vessel being furnished with its lid, and the stopper which closes the central opening being lifted up, the mixture is introduced by this opening in such quantity that the vessel be not

completely filled; a certain quantity of a mixture less charged with alcohol, and marking only 16° on the areometer of Beaumé, is then cautiously added. This, from its excess of density, falls to the bottom of the vessel, where it spreads itself in a horizontal layer. The oil is then introduced, which, by reason of the small excess of alcohol contained in the upper mixture, descends through the latter till it rests upon the denser layer of the lower mixture, either in a single mass or in several partial masses (§ 4). This being so, we unite, if the case requires it, the isolated spheres into a single one; then we stir the liquor cautiously with a glass rod, so as to mix imperfectly the layer at the bottom with the higher layers, but without dividing the mass of oil, and the system is then left to rest. It will be seen that there must hence result in the alcoholic liquor a state of density increasing from the upper layers of less density to the lower of greater density than that of the oil; and that, in consequence, the mass of oil will necessarily remain in stable equilibrium with respect to the vertical direction, in a certain layer whose mean density is equal to its own. Now, in performing the operation with the necessary precautions, that is to say by stirring the liquid only a very little, then leaving it to rest to observe the effect which results, again stirring it and leaving it to rest, and so on; lastly adding, if necessary, a small portion of mixture at 16°, or of pure alcohol, according to circumstances, we easily succeed in causing the mass of oil to remain exactly at the desired height, and, as we have seen, without tendency to a change of position in the vertical direction*. In geometrical strictness, truly, this mass of oil cannot then be any longer perfectly spherical: it must be flattened a little in the vertical direction; but, if we have operated so that the increase of the densities is very feeble at the height at which the oil stands,—and we easily obtain that result by suitable trials,—the flattening in question is completely insensible to the eye, and the mass appears exactly spherical.

For the experiments which we have to describe, the most convenient diameter to give to the sphere of oil is about 6 centimetres. We easily accomplish this by first forming a less sphere,

* The different liquid layers thus superposed tend of themselves, it is true, to mix; but, as they are placed in the order of their densities, this spontaneous mixture proceeds only with extreme slowness, and it requires a great many days for the liquor to become homogeneous. No inconvenience therefore results from this for the experiments.

and adding successively fresh portions of oil, which we unite with the first.

The next thing is to place the disc. This being attached by its axis to the rod which passes through the metallic stopper (§ 8), we begin by oiling it as well as the axis, then introduce it slowly into the alcoholic liquid, and cause it to penetrate by its edge into the sphere of oil. As the disc has previously been oiled, the sphere envelopes it without difficulty, and, what is remarkable, gradually of itself assumes such a position that the axis of the disc traverses it diametrically. This effect is evidently owing to the attractive action of this axis, or rather of the coating of oil with which it has been moistened,—an action which tends to operate in a symmetrical manner all around it, and thus brings the entire sphere of oil into a position symmetrical with respect to this same axis. Now it will be seen that the centre of the sphere tending, on the one hand, to remain at the height of that of the disc, on account of the superposition of the alcoholic layers of unequal density, and, on the other hand, to place itself in the axis of the disc, on account of the symmetry of the attractive actions exerted by the latter upon the oil, the centre of the sphere and that of the disc will coincide, and will thus remain in a fixed position. Only the sphere will then be slightly elongated in the vertical direction by the attraction of the axis of the disc; but this elongation is very trifling if the sphere present, as we have supposed, a diameter of 6 centimetres.

10. The sphere of oil being thus suitably placed, we slowly turn the handle. We then presently see the sphere *flatten at its poles and swell out at its equator*, and we thus realize on a small scale an effect which is admitted to have taken place in the planets.

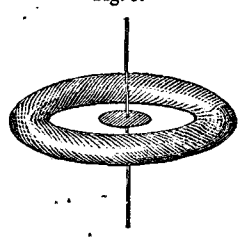
However, although the results may be of the same nature in the case of the great planetary masses and in that of our little masses of oil, I must not omit to remark here that there is an essential difference between the forces which are in play in the two cases. In the first, the force which tends to give to the great planetary mass a spherical figure, and against which the centrifugal force acts, is universal attraction; in the second, the force which acts the same part with regard to the small mass of oil, is molecular attraction, which is subject to different laws. But as, on either hand, the aggregate of the actions reduces itself to a contest between centrifugal force and another force

tending to preserve the spherical form of the liquid mass, it appears that the results must be analogous, if not identical, with respect to the figure which that mass assumes.

In order to observe in all its beauty the phænomenon on which we are engaged, the handle must at first be turned with very little velocity,—a turn in five or six seconds; the effects are then already very decided. If we afterwards apply a somewhat greater velocity,—for example, a turn in four seconds,—the flattening at the axis and the swelling at the equator are seen to be more considerable, and they are further augmented by increasing the velocity of the handle to one turn in three seconds. Before proceeding further, we may remark that in these experiments the handle must not be turned too long; for the mass of oil which in the first moments presents exactly a figure of revolution, eventually loses this form. At each fresh trial, therefore, the system must be left to repose; the oil then resumes its spherical form, and slowly, of itself, replaces itself in the proper position. The change of form which supervenes when too many turns are given to the disc, occasions results of a particular kind, and which are not without interest: I shall speak of them by-and-bye (§ 22).

11. Now, if instead of moving the handle slowly a considerable velocity is given to it, as two or three turns in a second, new and very curious phænomena are manifested. The liquid sphere first takes rapidly its maximum of flattening, then becomes hollow above and below around the axis of rotation, stretching out continually in a horizontal direction, and finally, abandoning the disc, is *transformed into a perfectly regular ring* (fig. 3).

Fig. 3.



This ring is rounded transversely, and appears to have a circle for its generatrix. At the moment of its formation its diameter increases rapidly up to a certain limit; when this is reached the movement of the disc must be stopped. The ring now remains for some seconds in the same state; then the resistance of the ambient liquid weakening its movement of rotation, it returns upon itself and changes back into a sphere around the disc and its axis.

The velocity of the handle most suitable for producing a beau-

tiful ring, is about three turns per second. The ring thus obtained has a mean diameter of 9 to 10 centimetres.

12. When, at the instant of the formation of the ring, the mass of oil which constitutes it separates from the disc, a singular circumstance is observable: the ring remains united to the disc by an extremely thin pellicle or film of oil, which fills all the space between them. But at the instant that, the ring having reached its greatest extent, we stop the motion of the disc, this pellicle breaks and disappears of itself, and the ring then remains perfectly isolated.

It may be conceived that this pellicle is not a circumstance essential to the phænomenon of the formation of the ring; and we shall see, in another part of these experiments, that it is probably connected with an order of facts wholly different.

13. The heavens exhibit to us also a body of a form analogous to our liquid ring. I allude to Saturn's ring. That, indeed, is flattened, whilst the transverse contour of ours appears altogether round; but I do not think that this difference is so great as it appears at first.

In fact, the centrifugal force, which goes on increasing from the inner circumference of the ring of oil up to its outer circumference, necessarily tends to stretch this ring in the direction of its breadth, or, in other words, to flatten it. But the flattening must be of very small amount; for, on account of the inconsiderable dimensions of the ring, and the slowness of its angular movement, the kind of traction which results from the variation of centrifugal force must be very trifling in comparison with the forces developed by molecular attraction.

14. It appears to me, then, that we may reasonably admit that our ring of oil is in reality slightly flattened, and that in consequence it only differs from that of Saturn, with regard to general form, in the less quantity of flattening*. But further, in the system of Saturn, the flattening of the ring is in part determined by the attraction of the central planet. Now, at the first moment of the formation of the ring of oil, the latter is submitted to a particular force, which plays a part analogous to that of the above attraction. In fact, this attraction acts with the greatest intensity at the inner circumference of Saturn's ring,

* I leave out of the question here the subdivision of the ring of Saturn; this subdivision, as is known, is not essentially connected with the conditions of equilibrium of the ring.

and thence decreases rapidly in the rest of this body. Now, at the first moment of the formation of the ring of oil, we have seen (§ 12) that the latter remains united to the disc by a thin film of the same liquid, and we may convince ourselves that this film exerts, on the inner circumference of the ring, a considerable force of traction. In fact, if we stop the movement of the disc a little too soon, that is to say a little before the ring has reached its maximum of diameter, the film of oil does not break, and the ring then returns upon itself (§ 11) with a much greater rapidity than when the film of oil is broken, and the ring remains isolated. The traction which the film of oil exerts on the inner circumference of the ring ought therefore to produce an effect analogous to that of the attraction of Saturn, that is to say, contribute to increase the flattening. Well, the ring of oil before the rupture of the film presents a very marked flattening. In order to obtain it perfectly, care must be taken that the sphere be well centred in relation to the disc, before beginning the experiment; and it is useful to turn the handle with a velocity somewhat less than that indicated at § 11: the most suitable velocity has appeared to me to be about two turns in a second. As soon as the film of oil breaks the flattening disappears, and the generatrix of the ring becomes, as we have seen, sensibly circular*.

* I had thought that it would be possible to obtain rings isolated and greatly flattened by operating upon larger masses of oil; for then the ring having a larger volume, the influence of the molecular attraction should be less. But I have found, that in operating on larger masses it was necessary, in order to obtain the ring in a regular manner, to employ a more feeble velocity of rotation; so that if the influence of the molecular attraction was diminished, that of the centrifugal force was so equally. The flattening then did not become more sensible, or if I have sometimes imagined that I observed any, I have not been able to reproduce it at will. I have operated thus on spheres which were successively about 10, 11, 12 and 14 centimetres in diameter, with discs of a diameter of from 7 to 9 centimetres, and in a vessel with plane surfaces, having a bottom 35 centimetres square, and a depth of 25 centimetres. The effects, however, thus obtained are very beautiful; the rings are magnificent, present a considerable diameter, and remain sometimes for eight to ten seconds before returning on themselves. With a sphere of 10 centimetres diameter, a disc of 7, and a velocity a little less than one turn of the disc per second, we obtain, in a very beautiful and very marked manner, the flattening resulting from the traction of the film of oil.

These experiments however are inconvenient and difficult, on account of the large dimensions of the vessel, and the great quantity of alcoholic liquid necessary to fill it.

It may be conceived, moreover, why a larger mass of oil requires a less velocity of rotation to produce a regular ring. It is precisely because the molecular attraction has less influence; whence it results that, if we attempt to em-

15. Geometricians who have investigated the figure of equilibrium of a liquid mass in rotation, have only regarded the case in which the attraction which counteracts the centrifugal force is that of universal gravitation, and they have demonstrated that elliptical figures in that case satisfy this equilibrium. Are we thence to conclude that the annular form developed by the rotation of our mass of oil results from the different law which governs molecular attraction (§ 10), and that, in the instance of the heavenly bodies, the figure of an isolated ring could not be produced by the sole combination of centrifugal force and of the mutual attractions of the different parts of the mass? I am not of that opinion, and I think it, on the contrary, very probable that if calculation could approach the general solution of this great problem, and lead directly to the determination of all the possible figures of equilibrium, the annular figure would be included among them. This general and direct solution presenting very great difficulties, geometricians have contented themselves with trying whether elliptical figures could satisfy the equilibrium, and with proving that they in fact do satisfy it; but they leave the question in doubt, whether other figures would not fulfill the same conditions. In truth, M. Liouville, in his last researches on this subject *, appears at first view to have nearly solved the question, by introducing the consideration of the stability of the figure of equilibrium, and showing that for each value of the moment of rotation, or, in other words, for any initial movement whatever of the mass, there is always an elliptical figure, either of revolution or of three unequal axes, according to the circumstances, which constitutes a form of stable equilibrium. It appears, in effect, natural to admit that for a given disturbance of a liquid mass there is but one single final state admissible; and in this case this state must necessarily possess stability. However, I do not deem the conclusion which may be drawn from these results so general as it appears at first sight. Without doubt, for a primitive disturbance given there is only one final state possible, and that state must be stable; but the condition of stability of a found figure of equilibrium does not necessarily involve the consequence that this

ploy the same velocity of rotation which would give a beautiful ring with a less quantity of oil, the mass disunites, and is scattered into spherules.

* The memoir of M. Liouville was communicated to the Academy of Sciences in the sitttng of the 13th of February in this year. An analysis of it may be found in the Journal *L'Institut*, No. 477.

figure will constitute the final state in question: for it may happen that several figures of equilibrium corresponding to the same primitive disturbance might equally possess stability, and that the choice of the mass for one of these figures may have been determined by other circumstances; for example, by the modifications which its movement experiences in the first moments of rotation. In fact, it is by examining these modifications, to which the attention of geometricians has not been directed, that I shall attempt to arrive at the mode of generation of annular figures.

16. When the mass begins to revolve upon itself, the angular velocity of the portions remote from the axis, which are carried off by their centrifugal force, necessarily goes on diminishing. This diminution is especially apparent on the equator of the mass, and it is the more considerable in proportion as the initial movement of rotation was more rapid. It thence results that in the first instants of a sufficiently rapid rotation there will be a great difference of angular velocity between the portions which are near the axis and those which are near the equator. Nevertheless, if we admit for a moment, that in virtue of the adherence of the liquid for itself, and of the friction of its several parts, the portions which turn most rapidly communicate by degrees a part of their velocity to the others, so that in the end the result is a mean angular velocity corresponding to the same moment of rotation, and equal in all the points of the mass, this may take an ellipsoidal figure. But long before the feeble forces of which we have just spoken can bring about this mean result, another order of phænomena would be manifested, which may impede the development of the elliptical figure and give rise to an annular form.

In fact, it follows necessarily from the preceding considerations that, in the first instants of a rotation sufficiently rapid, the centrifugal force at the equator of the mass will be much less than that which would correspond to the above mean velocity; and that, on the other hand, the centrifugal force of the portions near the axis will be by much superior to that which would correspond to the same mean velocity. The liquid next the axis will therefore be driven towards the liquid of the equator, whence there will necessarily result the formation of a sort of circular cushion (*bourrelet*), more or less marked. In other words, the mass will soon become hollow in the middle, and will

swell out all around. Now as soon as this phænomenon takes place, it will be conceived that the attraction exerted by this *bourrelet* on the liquid remaining around the axis must be an addition to the action of the centrifugal force, and contribute to increase the volume of the *bourrelet* at the expense of the central liquid. Hence, therefore, it may evidently result that all the liquid shall leave the axis for the *bourrelet*, and the latter become in a manner a veritable ring.

This generation of the annular figures would therefore be independent of the law which the attraction follows, and would be, in consequence, the same in the case of universal attraction and in that of molecular attraction.

17. It is easy to verify this mode of generation upon our mass of oil, or at least to assure ourselves that during the formation of the *bourrelet* and of the ring, the angular velocity is much less at the equator of the mass than towards the axis. For this purpose I shall first point out that when a certain number of experiments have been performed upon the same mass of oil, and this has been several times disunited and re-formed into a single sphere and into a ring, it always holds within it a multitude of small bubbles of alcoholic liquor, which, borne along by the oil that surrounds them, render the movements of the different points of the mass perfectly observable. Now, if the experiments which we have described be repeated with the aid of a sphere of oil thus filled with alcoholic bubbles, the following results are observed. So long as we give to the disc such slight velocities only as are sufficient to produce a simple flattening, there is not a great difference of angular velocity between the portions next to the axis and the portions adjoining the equator; but this difference becomes very considerable when the disc turns more rapidly, and the *bourrelet* and the ring are developed.

We may thus prove, by means of the small alcoholic bubbles, that the mean angular velocity is established in the ring once formed, and that all the points of the latter perform their revolutions in the same time.

Furthermore, in our experiments upon the masses of oil, there are two foreign forces which act, in addition to the causes which we have noticed, to facilitate the development of the *bourrelet* and of the ring. One is the resistance of the ambient liquid, which contributes to weaken the angular velocity of the equator of the mass; the other is the action of the hand which keeps up

the motion of rotation of the disc, and consequently hinders the central portions of the mass from participating gradually in the slackening of the equatorial portions. But that which is produced by these two foreign forces would be equally produced by a greater initial velocity of rotation if we could annul them.

18. When, by the aid of a moderate velocity of the disc, we limit ourselves to producing the flattening of the mass, the two foreign forces of which we have just spoken necessarily hin the latter from attaining an angular velocity equal in all its points, even though we keep turning the disc. The result is, that the mass cannot take exactly the figure which would correspond to that equality of angular velocity. That which it adopts is a figure of revolution; but on placing the eye at the height of the centre of the mass, it is easily recognised that it is not an ellipsoid; the curvature at the equator is too small, and this is the more evident in proportion as the flattening is more considerable.

Now, is this difference between the figure thus produced and that which would correspond to the case of universal gravitation solely the result of the action of the two foreign forces in question, or is it in part caused by the difference of the laws which the two kinds of attraction follow? In other words, if we could eliminate or render insensible the differences of angular velocity of the several parts of the mass of oil, would the figure produced be an ellipsoid or not? Now, we should render these differences of angular velocity insensible if we could impress a movement of rotation on a mass of oil suspended in an isolated manner, without interior system, in the alcoholic liquid, and then leave it to itself. In this case the resistance of the ambient liquid would be exercised indeed on the exterior of the mass; but nothing maintaining the constancy of velocity of the central parts, these, by virtue of the strong self-adherence of the oil, would participate eventually in the slackening of the exterior portions, and we might consider the mass as having each instant an angular velocity equal throughout.

Now, it is very easy to realize the above, by availing ourselves of the fact that, when the ring of oil is formed, it returns, after some time, upon itself (§ 11). At the instant when the ring is well developed, and when we have just stopt the disc, we lift the latter cautiously by means of the metallic stopper which bears its axis. Then the mass of oil, which is again

formed by the return of the ring upon itself, continues still to revolve for some time, completely isolated in the ambient liquid. Its figure is then, as well as the eye can judge of it, a perfect ellipsoid of revolution, which gradually approximates to a sphere in proportion as the rotatory motion becomes weaker *. Thus

* I had expected to be able to obtain a revolving isolated mass by means of another process, viz. by forming a sphere of oil in the middle of a cylindrical flask so arranged as to be able to turn upon its axis; then causing this flask thus to turn with rapidity, until all the liquid within, alcoholic mixture and mass of oil, had taken the same motion; then suddenly stopping the flask. In effect, it seems that then the alcoholic liquor being the first to lose its rotatory motion by the friction against the stationary sides of the flask, a moment must occur when the mass of oil maintains an excess of angular velocity over the ambient liquid, and that then the effects of centrifugal force upon that mass may manifest themselves. But the experiment gives few results. First, it is extremely difficult to keep a mass of oil in the middle of the flask. We keep it tolerably in the axis of the latter, because, if we have succeeded in placing it so that its centre is little removed from that axis, the rotation of the ambient liquid brings it there, and then retains it there very well. But it is not the same in the direction of the height of the flask. If a homogeneous alcoholic mixture be employed, and the sphere of oil is placed, before turning the flask, a little higher or lower than the middle of the height of the latter, it quits its place when the flask turns, to ascend, in the first case, or to descend, in the second, until it comes to be dispersed against one of the two bases of the flask. This effect is attributable, I think, to the fact that the two bases exercising upon the sections of liquid which touch them a motive action much greater than that to which the parallel sections of the interior of the mass are subjected, there ensues near these bases, at the commencement of the rotation, an excess of centrifugal force, which determines a tendency upwards and downwards of the liquid near the axis. It is therefore necessary to endeavour to place the sphere of oil in a position very near to the middle of the height of the vessel. Unfortunately we cannot use for this purpose the process of superposition of the alcoholic layers of unequal density (§ 9); for then, in the rotation of the flask, the denser inferior layers come necessarily, by the excess of centrifugal force which results from their excess of density, to rise against the sides, causing the less dense liquid to occupy the axis; and in this movement the mass of oil is drawn downwards, and is also dispersed upon the bottom of the vessel.

By employing a homogeneous alcoholic mixture and a sphere of oil of only about three centimetres diameter, I however succeeded several times, by dint of patience, in giving to this sphere a sufficiently exact position in the flask to be able to keep it at the same height until it had itself taken the rotatory movement of the whole system. But then, when I stopped the flask, a violent internal agitation was produced, which almost always dispersed the oil in innumerable spherules throughout the alcoholic liquid, or at least destroyed its form in a completely irregular manner. I attribute these effects to the following cause. When the flask is stopt, the portions of the alcoholic liquid which touch the sides and bases, losing first their centrifugal force, the more internal portions, which still retain theirs, make their way through them, dividing them, and this confusion is soon propagated to the axis, where it gives rise either to the dispersion or to the irregular disfiguring of the mass of oil.

In the cases in which I have been able to give a suitable position to the sphere of oil, I have observed a curious effect; namely, that in the first instants of the rotation of the vessel the mass of oil quits the spherical form, and becomes elongated in the direction of the axis of rotation. This elongation is

the difference of the laws which govern the two sorts of attraction appears not to influence the nature of the figure taken by the mass that turns upon itself.

19. A liquid mass can only assume and preserve an annular form under the influence of a sufficient centrifugal force. Thus, as we have seen, when the resistance of the alcoholic liquid has diminished below a certain limit the velocity of rotation of the ring of oil, the latter, obeying the preponderating action of the molecular attraction, returns upon itself, loses its annular form, and re-constitutes itself into an entire mass, first ellipsoidal and then spherical. But if, by a method which I shall describe, we prevent the ring from agglomerating thus, and still leave the action of its centrifugal force to diminish, we then witness the appearance of other phænomena well meriting interest. In order to produce them perfectly, in place of the disc of 35 millimetres, a disc of about 5 centimetres in diameter must be substituted*, which renders necessary, in order to form the ring well, a less velocity of rotation than with the preceding disc (the most suitable appears to me to be a little less than two turns in a second). Now, instead of stopping the movement of the disc at the instant when the ring has attained its greatest development, we must continue to move the handle. The film of oil will then break in a little time, as if the disc had been stopt; but the latter continuing to revolve in the alcoholic liquor, the portions of that liquor which are in contact with it will themselves assume a rotatory movement, and the centrifugal force which results from it will drive them continually towards the ring, so that the latter will not be able to return upon itself. Now, in these circumstances, we

easily explained: the movement of rotation is communicated to the portions of the mixture which are nearest the axis above and below the mass of oil, before being able to communicate itself with the same intensity to the latter: hence, in the different points of this mass, there must result a less centrifugal force than in the points of the alcoholic mixture situated at the same distances from the axis of rotation. Thence a rush of the oil to the axis, and an elongation of the mass of the latter in the direction of this same axis. But, on continuing the rotation, the oil comes to receive the same movement as the surrounding liquid, and it also resumes gradually the spherical form.

On stopping the flask, not suddenly, but in a rather rapid manner, I succeeded once in obtaining a result sufficiently regular, and I observed, as I expected, the sphere become flattened considerably in the direction of the axis of rotation.

* This substitution is accomplished by detaching the upper end of the axis of the first disc from the large wire which passes through the metallic stopper (§ 8), and screwing in its place the end of the axis of the new disc.

soon see the ring lose its regularity, then divide into several isolated masses, each of which immediately takes the spherical form. Thus the ring, when it cannot preserve its figure on account of the decrease of its centrifugal force, and an obstacle prevents its reforming itself into a single sphere, resolved itself into several isolated spheres. As soon as the separation begins to take place, the movement of the disc must be stopt.

This is not all: one or more of these spheres are then almost always seen to assume, at the instant of their formation, a movement of rotation upon themselves,—a movement which constantly takes place in the same direction as that of the ring. Moreover, as the ring, at the instant of its rupture, had still a remainder of velocity, the spheres to which it has given birth tend to fly off at a tangent; but as, on the other side, the disc, turning in the alcoholic liquor, has impressed on this a movement of rotation, the spheres are especially carried along by this last movement, and revolve for some time around the disc. Those which revolve at the same time upon themselves consequently then present the curious spectacle of planets revolving at the same time on themselves and in their orbit. The movement of rotation of these masses is, however, too slow in relation to their diameter to cause any sensible flattening. Finally, another very curious effect is also manifested in these circumstances: besides three or four large spheres into which the ring resolves itself, there are almost always produced one or two very small ones, which may thus be compared to satellites.

The experiment which we have just described presents, as we see, an image in miniature of the formation of the planets, according to the hypothesis of Laplace, by the rupture of the cosmical rings attributable to the condensation of the solar atmosphere.

20. When some oil is introduced into a mixture containing a little excess of alcohol, a phænomenon is observable which is connected with that of the resolution of the ring into isolated spheres. If the oil be poured in with sufficient rapidity, it forms a long cylindrical train extending from the beak of the funnel to the bottom of the vessel, where the mass gathers. Now, this kind of tail which connects the mass of oil with the beak of the funnel remains as long as the oil which forms it has a sufficiently rapid movement of translation, that is to say, as long as we con-

tinue to pour; but as soon as we cease to pour out and the movement of translation is slackened, the train of oil is instantly resolved into several isolated spherules.

21. The formation of a ring analogous to that of Saturn naturally inspires the desire to carry further the resemblance to the system of that planet, and to seek whether, by some modification of our experiment, it would not be possible to contrive so that a sphere of oil should remain in the middle of the ring. Now, I have succeeded in producing this effect, by means of a process which I shall proceed to describe; only that this experiment must be regarded merely as a scientific sport, for the circumstances which give rise to the result have evidently no analogy with those which can have occasioned the configuration of the system of Saturn.

It is first necessary to be able to give to the disc a considerable velocity of rotation. To do this, we adapt to the upper part of the vessel a system of two pulleys, one small, and fixt on to the prolongation of the axis of the disc at the place of the handle, which is taken away; the other larger, and to the axis of which the same handle is attached. In my apparatus the diameters of the two pulleys are respectively 12 and 75 millimetres. In the second place, the diameter of the sphere being always nearly 6 centimetres, that of the disc should be only 2 centimetres. Lastly, the disc should not have, as in the preceding experiments, its centre coinciding with that of the sphere, it should be placed lower, toward the inferior part of the latter.

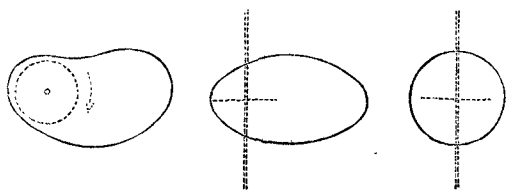
Matters being thus arranged, the handle is turned with a velocity which experience soon enables us to find: in my apparatus this velocity ought to be about two turns and a half per second, which nearly corresponds to fifteen turns of the disc in the same time. We then see, in general, a ring rapidly formed, which extends itself, leaving in its centre a mass of oil, to which it remains united by a thin pellicle. At the instant when the ring has attained a sufficient development (and by habit alone can this be correctly learnt), the rotation is suddenly stopt. The pellicle then breaks, the ring remains completely isolated, and the central mass forms into a sphere. We have thus, during some instants, a curious representation of the system of Saturn, except the flattening of the ring. The ring returns rapidly afterwards upon itself, and is again united to the central sphere.

This experiment does not offer any great difficulties; it requires however some skill to succeed perfectly*.

22. In describing (§ 10) the experiment in which the flattening of the sphere is effected by the immediate action of the disc, I have remarked that the movement of the latter should not be continued too long, because the mass of oil then comes to lose its form. Now, if we continue, nevertheless, to turn the handle, with a view to observe the results of this disfigurement, we see manifested new and very capricious effects.

The sphere being well centred with relation to the disc, if we give velocities of one turn in six, five or four seconds to the latter, we begin, after seven or eight turns, to see the mass of oil elongate itself horizontally in one direction, taking a form which resembles much an ellipsoid of three axes; and, what is more singular, this kind of ellipsoid is placed in an eccentric manner with relation to the axis of rotation. Figure 4 represents, for a

Fig. 4.



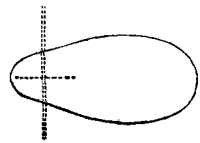
velocity of a turn in four seconds, the mass viewed from three different sides; that is to say, from above and in the two lateral directions of the smallest and of the largest horizontal axis: the dotted parts indicate the positions of the disc and of the axis of rotation. The aspect of the mass seen from above shows that it is slightly bent in one direction; but this effect is evidently owing to the resistance of the ambient liquid.

When once the mass has taken this form, it preserves it indefinitely as long as the movement of the disc continues; it continues to revolve eccentrically round the latter, and with a velocity much less than that of this disc. This inferior velocity, I may add, evidently also proceeds from the resistance of the ambient liquid.

* On communicating this very experiment to the Academy, in the sitting of April 1842 (see the *Bulletins*), I stated that it was necessary to vary the velocity of rotation. I have since found that having adopted a convenient velocity, it was best to keep it uniform.

If a greater velocity is given to the disc, without however passing a certain limit, —if, for example, we give it one turn in three seconds,—the phænomena are still of the same kind; only the mass is more elongated, the flexure due to the resistance of the ambient liquid is more decided, and the form is more removed from an ellipsoid. Figure 5 represents the mass viewed on the side, and showing to the eye its greatest length.

Fig. 5.



If the velocity of the disc is increased to a turn in two seconds, the phænomena become less constant and less regular; we should say that there is, for this velocity, a transition from one order of phænomena to another, and that the mass hesitates between the two.

In fact, with a velocity still a little greater, namely about one turn in a second and a half, the phænomena begin again to be regular and constant, but they are different from the first. They are exhibited in all their beauty when the velocity is increased to a turn in a second. The mass then is at first deeply hollowed around the axis, as if the ring was on the point of being developed; and it remains under this form of a circular *bourrelet* during sixteen to eighteen turns of the disc; we then see it elongate gradually according to a horizontal diameter, but no longer eccentrically, so that, seen from above, it presents an elliptic figure sometimes very perfect, of which the disc occupies the centre (fig. 6). This ellipse then lengthens more and more,

Fig. 6.

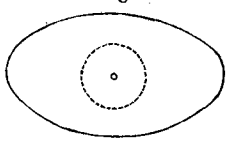
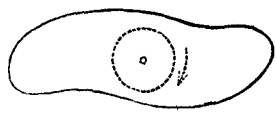
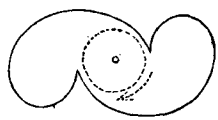


Fig. 7.



rather rapidly, and begins to bend by the resistance of the ambient liquid (fig. 7). Lastly, on a sudden the mass becomes strongly inflected from both sides, and its form seen from above is then as represented in figure 8. The mass afterwards preserves this last form in a perfectly fixed manner, as long as the movement of the disc continues.

Fig. 8.



23. However capricious these phænomena may appear, chance

or accidental causes have still no part in them. I have repeated a great number of times the experiments detailed above, and the effects have always been identically the same for the same velocities.

After having seen the stable figures which the mass takes in these circumstances, we cannot help making a comparison between these figures and the ellipsoids of three axes of MM. Jacobi and Liouville (§ 15),—ellipsoids which are also always, as the latter of these geometricians has shown, figures of stable equilibrium. Would the identity of the phænomena in the case of universal gravitation and in that of molecular attraction hold good so far? Doubtless the singular figures which we have just described are not ellipsoids; but their aspect admits of our attributing the difference to the resistance of the ambient liquid, which on one side determines the flexures of which we have spoken, and on the other maintains a permanent inequality of angular velocity between the portions adjoining the disc and the more distant portions. Calculation alone could inform us up to what point the above comparison is well founded; the complete solution of the problem, for the case of molecular attraction, would perhaps not present difficulties so insurmountable as for that of universal attraction.

24. In all the experiments which I have described in this memoir, I have supposed that the oil and the alcoholic mixture were rendered chemically inert with regard to each other, and I have said (§ 6) that it was easy in a short space of time to obtain two such liquids. I proceed now to detail the process by means of which this object is attained.

We begin by making a mixture of alcohol and distilled water, containing a certain excess of alcohol, so that when submitted to the trial of the test tube (§ 3) it lets the small sphere of oil fall to the bottom rather rapidly. After having formed the mixture in quantity more than sufficient to fill the vessel which is to serve for the experiments, we introduce into this same mixture a quantity of oil about double what is considered necessary for these experiments *. If a flask is not at hand large enough to contain the whole, we divide the masses among several separate flasks: but care must then be taken that each one may contain

* It is indispensable to have the two liquids thus in excess, on account of the quantities which are necessarily lost during the different operations which we shall describe, and in the preparation of the experiments.

the same proportions of water, alcohol and oil. After this we invert these flasks rapidly a great number of times, but without shaking them, until the oil has been divided into spherules of the size of a pin's head: the whole is then left to rest. Then, if the alcohol of the mixture is in proper quantity, the spherules should sink with extreme slowness, so as to take about a quarter of an hour for the greater part to collect at the bottom of the flasks. If it is otherwise, water or alcohol is to be added as may be required, the contents to be mixed by inverting the flasks several times, as above, then left again to settle, and the operation thus to be recommenced until the result is obtained which I have described. When this point is obtained, the whole is thrown upon filters, care being taken to cover the funnels containing these last with plates of glass; this precaution is necessary in order to prevent as much as possible the evaporation of the alcohol, and for another reason of which we shall speak hereafter. The alcoholic liquor passes the first through the filters, ordinarily carrying with it a certain number of very minute spherules of oil. When the greater part has thus passed, the spherules become more numerous; what still remains in the first filters, namely the oil and a residue of alcoholic liquor, is then thrown into a single filter placed on a new flask. This last filtration takes place much more slowly than the first, on account of the viscosity of the oil; it is considerably accelerated by renewing the filter once or twice during the operation. If the funnel has been covered with sufficient care, the oil will collect into a single mass at the bottom of the flask, under a layer of alcoholic liquor.

The preceding operations have thus given us the following results:—on the one hand the inert alcoholic mixture, still holding a small excess of alcohol, and containing a certain number of small spherules of oil; on the other hand, the oil equally inert, and covered with a little of this same alcoholic liquid. Now, a second filtration completely clears the first from the spherules which it holds; with respect to the oil, it is extracted from below the alcoholic layer by means of a small siphon armed with a lateral tube, and received into a dry flask which is to be perfectly corked. In this manner we have the two liquids separate, and inactive with regard to each other. When it is desired to use them, if we perceive that the alcoholic liquid is a little too dense, we correct it with pure alcohol; and if, on the contrary,

there is too little density, we correct it with alcohol at 16 degrees. In this latter case we must not use pure water, because this, when it mixes with the prepared alcoholic liquor, produces in it a cloudiness more or less decided.

The various trials I have made relatively to the above process, have led me to ascertain that the two liquids, when they have not been submitted to this preparation, are both modified by their mutual contact. The alcoholic liquid dissolves some oil, and this in its turn probably dissolves some alcohol. It is especially from the modification which the oil undergoes that its great diminution of relative density results (§ 6). Now, when the oil thus modified remains exposed to the air, it passes again gradually to the state of fresh oil, and resumes its former density. It is partly to avoid this that I have recommended the funnels which enclose the filters to be kept constantly covered, and the oil to be kept in a flask perfectly corked. As for the alcoholic mixture, it is evident that this last precaution is equally necessary.

25. Before I conclude, I must forewarn those persons who may wish to repeat my experiments, of two effects which sometimes occur, and which cause disturbance in the operations if the experimenter does not know the means of preventing or destroying them.

When some oil is introduced into a mixture containing an excess of alcohol, it happens sometimes that the mass which has sunk to the bottom of the vessel contracts adherence with this bottom and spreads itself out more or less on its surface. There is then no means of removing it entire; but the spreading of the adhesion may be prevented by contriving that the bottom of the vessel should be occupied by a layer of a mixture more dense than the oil (§ 9).

The second effect to which I allude is presented in the inverse case, that is to say, when the sphere of oil, instead of reaching the bottom of the vessel, rises, on the contrary, to the surface of the alcoholic liquor, either because this liquor contains too little alcohol, or on account of a lowering of temperature, or because we have not been able to use prepared oil. When this happens, the mass flattens at first more or less at the surface of the mixture, as if this last opposed a resistance to it; then, after some time, it makes its way through, and then presents a portion of plane surface, more or less extended, on the level with

that of the alcoholic liquor. But what occasions trouble is, that then, so to speak, it has contracted an adherence with this same surface, from which it is not detached without great difficulty. It is at first easy to prevent the production of this effect by pouring on the surface of the liquor a small layer of pure alcohol; and this same means will serve also to destroy the effect in question, if it is already produced. In this latter case we may again invert the vessel with caution: the movement thus imparted to the ambient liquor suffices ordinarily to detach the mass of oil, with the exception of a small portion, which almost always remains adhering to the surface.

26. Lastly, I have already mentioned the fact, that after a certain number of experiments the oil becomes filled with small spherules of alcoholic liquor. Now, reciprocally, the ambient alcoholic liquor is also often sprinkled with a multitude of small spherules of oil. It is scarcely necessary to remark that when all these spherules have become too numerous, and we desire to restore the liquids to their original transparency, this is easily accomplished by filtrations similar to those of which I have spoken above (§ 24).

27. We have been hitherto engaged with the figures assumed by a liquid mass abstracted from the action of gravity and submitted to the attraction of its molecules, either when this mass is at rest, or when a movement of rotation upon itself is imparted to it. Notwithstanding the difference of the laws which the attractive forces follow in this case and in that of the large planetary masses, we have seen produced, on a small scale, a striking representation of the majority of the phænomena of configuration relative to the celestial bodies. In the second part of this investigation we shall submit our liquid masses to new forces, and we shall then see developed a series of phænomena quite as curious but of a different class.

NOTE.

[Professor Faraday, who has repeated many of M. Plateau's remarkable and beautiful experiments, informs me that he coloured his oil green, for the purpose of rendering it more distinctly visible in the spirit, by dissolving in it a little oxide of copper. This, he states, is easily done by heating a little oil with the oxide, and then mingling that with the rest.—ED.]

Article III.

Memoir on the Solar Heat, on the Radiating and Absorbing Powers of the Atmospheric Air, and on the Temperature of Space. *By* M. Pouillet, *Member of the Royal Academy of Sciences of Paris, Professor of Natural Philosophy in the Faculty of Sciences, &c.*

[From the *Comptes Rendus des Séances de l'Académie des Sciences*, July the 9th, 1838.]

THE object of this memoir is—the quantity of solar heat which falls perpendicularly, in a given time, on a given surface:—the proportion of this heat which is absorbed by the atmosphere in the vertical passage:—the law of absorption for different ob liquities:—the total quantity of heat which the earth receives from the sun in the course of a year:—the total quantity of heat which is emitted at each instant by the whole surface of the sun:—the elements which must be known in order to ascertain whether the mass of the sun cools gradually from century to century, or whether there is a cause destined to reproduce the quantities of heat which escape incessantly from it:—the elements which would allow its temperature to be determined:—the absolute quantity of heat emitted by a body whose surface, temperature and radiating power are known:—the laws of cooling of a body which loses its heat without receiving any:—the general conditions of equilibrium of temperature of a body protected by a diathermanous covering analogous to the atmosphere:—the cause of the cooling of the high regions of the air:—the law of that cooling:—the temperature of space:—the temperature which would be observable everywhere on the surface of the earth if the sun's action was not felt:—the elevation of temperature which results from the solar heat:—the relation of the quantities of heat which the earth receives from the sun, and from space or all the other celestial bodies.

It is difficult to give a brief account of the whole of these researches: I must therefore be excused both for the length of this abstract and the conciseness with which many of the propositions are presented. I regret to be unable here to go more fully into the subject, and especially that I cannot review the

labours of those who have preceded me, particularly those of M. de Laplace, M. Fourier and M. Poisson.

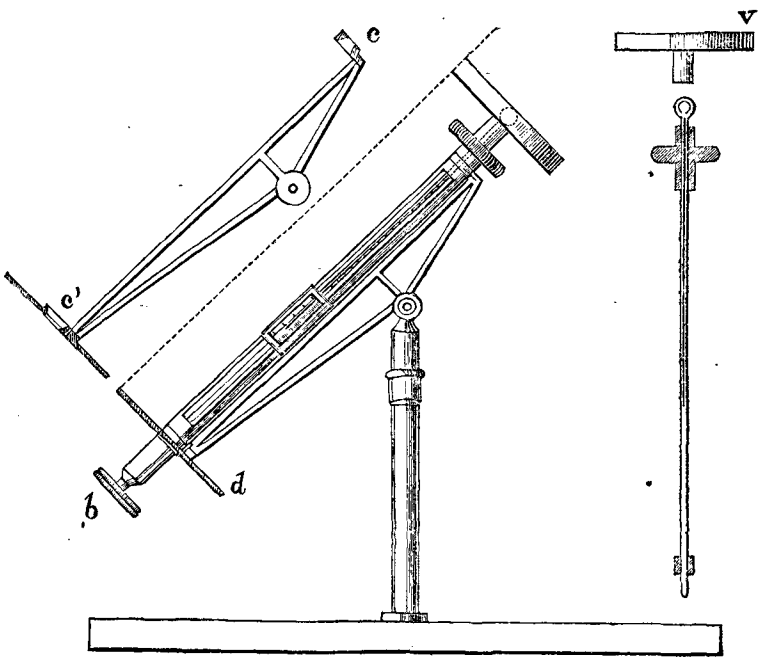
1. I have attempted to determine the quantity of solar heat by three different processes :—

(1.) By means of the apparatus which is described in the two first editions of my *Elémens de Physique et de Météorologie.*

(2.) By means of a direct pyrheliometer.

(3.) By means of a pyrheliometer with a lens.

The direct pyrheliometer is represented in the annexed figure.



The vessel V is very thin, of silver or plated metal: one decimetre in diameter, and 14 or 15 millimetres high; it contains about 100 grammes of water. The stopper which fixes the thermometer to the vessel is fitted to a metal tube which is supported at its extremities by two collets c, c', in which it plays freely; so that on turning the button b, the whole apparatus turns round the axis of the thermometer, and the water of the vessel is incessantly agitated in order that the temperature may

be very uniform in its whole mass. The circle d, which receives the shadow of the vessel, serves to adjust the apparatus. The surface of the vessel which receives the solar action is carefully blackened with lamp-black.

The experiment is made in the following manner:—The water in the vessel being nearly of the surrounding temperature, the pyrheliometer is held in the shade, but very near the place where it is to receive the sun: it is placed so that it looks towards the same extent of sky; and there, for four minutes, its warming or its cooling is noted from minute to minute; during the following minute it is placed behind a screen, and then adjusted so that on removing the screen at the end of the minute, which will be the fifth, the solar rays strike it perpendicularly. Then, during five minutes, under the action of the sun, its warming, which becomes very rapid, is observed from minute to minute, and care is taken to keep the water incessantly agitated; at the end of the fifth minute the screen is replaced, the apparatus withdrawn into its first position, and for five minutes more its cooling is observed.

Let R be the warming which it undergoes during the five minutes of the solar action, r and r' the coolings which it underwent during the five minutes which preceded that action and during the five minutes which followed it, it is easy to see that the elevation of temperature t produced by the heat of the sun is

$$t = \mathrm{R} - \frac{(r + r')}{2}.$$

Let d be the diameter of the vessel expressed in centimetres, p the weight of the water which it contains expressed in grammes, p' the weight of the vessel itself and of the immersed portion of the thermometer, this weight being reduced to what it would be for a specific heat equal to unity, we see that the elevation of temperature observed t, corresponds with a quantity of heat

$$t\,(p + p').$$

This heat having fallen in five minutes on a surface $\frac{\pi d^2}{4}$, each unity of surface has received

$$\frac{4\,(p + p')}{\pi d^2}\,t \text{ during the five minutes,}$$

and

$$\frac{4\,(p + p')}{5\,\pi d^2}\,t \text{ during one minute.}$$

In my apparatus this quantity of heat received in one minute by each square centimetre is

$$0{\cdot}2624\,t.$$

The pyrheliometer with a lens consists of a lens of 24 to 25 centimetres diameter, having a focal distance of 60 to 70 centimetres, in whose focus is placed a silver or plated vessel containing about 600 grammes of water; the form of the vessel and the arrangement of the lens are so combined that for all heights of the sun the rays fall perpendicularly on the lens and on the face of the vessel which is to receive them at the focus and to absorb them.

The experiments are performed as with the preceding apparatus, and the quantities of heat which fall in one minute on each square centimetre are determined by an analogous formula; only there is an additional correction to be made for the quantity of heat which the lens absorbs, and that correction is made by the comparison of the results obtained with the lens and with the direct apparatus. Among the lenses which I have tried, that which absorbed the least nevertheless absorbed one-eighth of the incident heat.

It is necessary to employ the pyrheliometer with a lens when the experiments cannot be made in a calm air; the wind, when it is not strong, has but small influence in cooling within five minutes a mass of water of more than 600 grammes, which is raised only four or five degrees above the surrounding temperature, so that the correction is always very small.

2. The following table contains five series of experiments, which will give a sufficient idea of the variations of the direct pyrheliometer. The elevations of temperature observed are in the third column. We shall show hereafter how the numbers of the second and fourth columns have been obtained.

Hours of Observation.	Atmospheric Densities, or δ.	Observed rises of Temperature.	Calculated rises of Temperature.	Differences.
	Observations of the 28th of June, 1837.			
7h 30′ morn.	1·860	3°·80	3°·69	+0·11
10h 30′ morn.	1·164	4·00	4·62	−0·62
Noon	1·107	4·70	4·70	0·
1h.....	1·132	4·65	4·67	−0·02
2	1·216	4·60	4·54	+0·06
3	1·370	.....	4·32	0·
4	1·648	4·00	3·95	+0·05
5	2·151	.....	3·36	
6	3·165	2·40	2·42	−0·02
	Observations of the 27th of July, 1837.			
Noon	1·147	4·90	4·90	0·
1h.....	1·174	4·85	4·86	−0·01
2	1·266	4·75	4·74	+0·01
3	1·444	4·50	4·51	−0·01
4	1·764	4·10	4·13	−0·03
5	2·174	3·50	3·49	+0·01
6	3·702	3·35	3·42	−0·07
	Observations of the 22nd of September, 1837.			
Noon	1·507	4·60	4·60	0·
1h.....	1·559	4·50	4·54	−0·04
2	1·723	4·30	4·36	−0 06
3	2·102	4·00	3·97	+0·03
4	2·898	3·10	3·24	−0·14
5	4·992	.....	1·91	
	Observations of the 4th of May, 1838.			
Noon	1·191	4·80	4·80	0·
1h.....	1·223	4·70	4·76	−0·06
2	1·325	4·60	4·62	−0·02
3	1·529	4·30	4·36	−0·06
4	1·912	3·90	3·92	−0·02
5	2·603	3·20	3·22	−0·02
6	4·311	1·95	1·94	+0·01
	Observations of the 11th of May, 1838.			
11h.....	1·193	5·05	5·06	−0·01
12	1·164	5·10	5·10	0·
1	1·193	5·05	5·06	−0·01
2	1·288	4·85	4·95	−0·10
3	1·473	4·70	4·73	−0·03
4	1·812	4·20	4·37	−0·17
5	2·465	3·65	3·67	−0·02
6	3·943	2·70	2·64	+0·06

3. After having obtained, in the course of several years, a large number of series analogous to the preceding, I endeavoured to discover a law which might represent with sufficient exactness

all the results of the observations. To effect this, I first calculated the atmospheric thicknesses which the solar rays had to traverse in each experiment; these thicknesses ε are given by the formula

$$\varepsilon = \sqrt{2rh + h^2 + r^2\cos^2 z} - r\cos z;$$

r is the mean radius of the earth, h the height of the atmosphere, z the zenithal distance of the sun; I adopted

$$h = 1, r = 80.$$

With respect to the zenithal distance z, instead of determining it each time by observation of the sun's altitude, I preferred to take the precise hour of the middle of the experiment, and to deduce the value of z from the formula

$$\cos z = \sin v \sin d + \cos v \cos d \cos \mathrm{H}.$$

v is the latitude of the spot where the observation is taken, d the declination of the sun at noon, H the horary angle of the sun corresponding to the hour of the experiment.

By means of these two formulæ I calculated the atmospheric thicknesses given in the second column of the preceding table.

4. By comparing the elevations of temperatures observed on the pyrheliometer and the corresponding atmospheric thicknesses, I saw that the results might be very well represented by the formula

$$t = \mathrm{A}p^{\lambda},$$

A and p being two constants. Moreover, by determining these two constants by two observations of each series, we always obtain the same value of A for all the series, and different values of p in passing from one series to the other. Thus A is a fixed constant, independent of the state of the atmosphere, and p a constant which is fixed only for the same day, and which varies from one day to another, according as the serenity of the sky is more or less perfect. A is therefore, in the formula, the *solar constant*, or that which contains, as its essential element, the constant calorific power of the sun, whilst p is the atmospheric constant, or that which contains, as its essential element, the power of variable transmission, which the atmosphere possesses to allow portions of the incident solar heat, more or less great, to arrive at the surface of the earth.

The experiments give for A the value

$$6^{\circ}.72,$$

and for p the values contained in the following table:—

Dates of the Series.	Values of p.	Values of $1-p$.
June 28	0·7244	0·2756
July 27	0·7585	0·2415
September 22 . . .	0·7780	0·2220
May 4	0·7556	0·2444
May 11	0·7888	0·2112
Winter solstice	0·7488	0·2512

By means of these values of A and of p, and of the formula

$$t = \mathrm{A}p^{s},$$

I calculated the results contained in the fourth column of the preceding table; it is seen with what accuracy all the numbers which had been given by observation are thus reproduced, even when the observation corresponds to atmospheric thicknesses, which are quadrupled by the effect of obliquity. Thus in the experiments of the 4th of May, the solar rays had to traverse an atmospheric thickness of 24 leagues at noon, and 86 leagues at six o'clock in the evening, and yet the number calculated is still found perfectly to agree with the number observed. It is understood, however, that it is only when the weather is quite settled that the formula can be applied with accuracy to an entire day with the same value of p; if there occur any sudden changes in the state of the atmosphere, the values of p immediately experience a greater or less alteration: I have succeeded in convincing myself of this by a multitude of experiments corresponding to all the seasons of the year. It may even be assumed that in certain spots, especially in mountainous countries and near the sea-coast, the values of p undergo every day periodical variations, corresponding to the diffusion and to the condensation of the vapours.

5. If in the preceding formula we suppose $p = 1$, or $s = 0$, we find

$$t = 6°{\cdot}72;$$

that is to say, that the pyrheliometer would assume an elevation of 6°·72 if the atmosphere could transmit wholly all the solar heat without absorbing any of it, or if the apparatus could be transported to the limits of the atmosphere to receive there without any loss all the heat which comes to us from the sun. This value of t multiplied by 0·2624, gives

$$1{\cdot}7633.$$

This then is the quantity of heat which the sun gives in 1′ on a square centimetre, at the limits of the atmosphere, and which

it would equally give at the surface of the earth, if the atmospheric air did not absorb any of the incident rays.

6. The preceding values of p indicate the proportions of solar heat which have been transmitted in the different days to which they correspond, and the values of $1-p$ indicate, on the contrary, the different proportions of solar heat which have been absorbed at the same periods. These values, however, correspond to $\varepsilon = 1$, that is to say, they indicate the proportions of solar heat which would have been transmitted and absorbed at those places where the sun was in the zenith, supposing there the same atmospheric state as at Paris at the moment of the experiment. It results that in the vertical passage the atmosphere absorbs at least $\frac{21}{100}$ of the incident heat, and at most $\frac{27}{100}$, without the sky ceasing to be serene. I must however add, that on the 28th of June, to which corresponds the absorption of $\frac{27}{100}$, a light white veil was visible on the vault of the sky. Moreover other observations, the series of which could not be completed, indicated only an absorption of $\frac{18}{100}$; we may thus say that the atmospheric absorption is comprised between 18 and 24 or 25 hundredths, without its being possible to distinguish in the sky vapours which disturb its transparence.

7. By means of this datum, and of the law according to which the transmitted heat diminishes in proportion as the obliquity increases, we may calculate the proportion of incident heat which each instant reaches the illuminated hemisphere of the earth, and that which is absorbed in the corresponding half of the atmosphere. This calculation depends on an integral of the form

$$c\int\frac{p^{\varepsilon}\,d\varepsilon}{\varepsilon^2},$$

which cannot be obtained exactly; but by various methods of approximation, it is easy to recognise that for $p = 0{\cdot}75$ the proportion which reaches the ground is comprised between 0·5 and 0·6, and consequently the proportion absorbed by the atmosphere is itself comprised between 0·5 and 0·4; but very near 0·4.

Thus, when the atmosphere has all the appearance of perfect serenity, it still absorbs nearly the half of the total quantity of heat which the sun emits towards the earth, and it is the other half only of that heat which falls upon the surface of the ground, and which is there variously distributed, according as it has traversed the atmosphere with greater or less obliquities.

8. Having ascertained the quantity of heat which the sun sends to the earth during 1′, by its perpendicular action upon a square centimetre, it is easy to determine the total quantity of heat which the entire globe of the earth and the atmosphere receive each minute. In fact, that quantity of heat is what would fall upon the circle of illumination if the hemisphere of the earth, which is at the same time illuminated and heated by the sun, were removed. Now the surface of this circle of illumination being πR^2, the total quantity of heat which it receives is

$$1{\cdot}7633 \,.\, \pi R^2.$$

If this heat were uniformly dispersed over all points of the earth, each square centimetre would receive for its share only

$$\frac{1{\cdot}7633 \,.\, \pi R^2}{4 \pi R^2} \text{ or } 0{\cdot}4408.$$

It is easy to see, according to this, that in the course of a year the total quantity of heat received by the earth from the sun is the same as if, during that interval, there should enter, by each square centimetre of the surface which limits the atmosphere,

231675 unities.

By transforming this quantity of heat into a quantity of melted ice, we obtain the following result:—

If the total quantity of heat which the earth receives from the sun in the course of a year were uniformly dispersed over all points of the globe, and if it were there employed, without any loss, in dissolving ice, it would be capable of dissolving a stratum of ice which would envelope the whole earth, and which would have a thickness of

$$30^{m}{\cdot}89,$$

or nearly 31 metres; such is the simplest expression of the total quantity of heat which the earth receives every year from the sun.

9. The same fundamental datum enables us to solve another question, which will perhaps appear more bold, and the solution of which is nevertheless quite as simple. It enables us to find the total quantity of heat which escapes from the entire globe of the sun in a given time, without supposing anything, except that all the equal portions of the globe of the sun emit equal quantities of heat; this appears hitherto confirmed by experiment, since the different aspects which the sun presents to us

by the effect of its rotation do not appear to have any marked influence upon the terrestrial temperatures.

Let us consider the centre of the sun as the centre of a spherical inclosure, the radius of which is equal to the mean distance of the earth to the sun: it is evident, that upon this vast inclosure every square centimetre receives in 1′ from the sun precisely as much heat as the square centimetre of the earth, that is to say 1·7633; consequently, the total quantity of heat which it receives is equal to its entire surface, expressed in centimetres and multiplied by 1·7633, or to $1{\cdot}7633 \cdot 4\pi D^2$.

This incident heat is nothing else than the total sum of the quantities of heat emitted in all directions by the entire globe of the sun, that is to say by a surface $4\pi R^2$, R being the radius of the sun. Thus each square centimetre emits for its share

$$1{\cdot}7633 \cdot \frac{D^2}{R^2} \text{ or } \frac{1{\cdot}7633}{\sin^2 \omega};$$

ω being the visual demi-angle at which the sun is seen from the earth, that is to say 15′ — 40″; which gives 84888: thus each square centimetre of the solar surface emits in 1′

84888 unities of heat.

By transforming this heat into a quantity of melted ice, we obtain the following result:—

If the total quantity of heat emitted by the sun were exclusively employed in dissolving a stratum of ice applied upon the globe of the sun, and enveloping it on every side, that quantity of heat would be capable of dissolving in 1′ a stratum of $1^m{\cdot}80$ thick, and in one day a stratum of 16992^m, or $4\frac{1}{4}$ leagues. This determination, as will have been seen, does not rest upon any hypothesis; it is independent of the peculiar nature of the sun, of the matter of which it is composed, of its radiating power, of its temperature and of its specific heat; it is simply the immediate consequence of the principles best established in relation to radiating heat, and of the number which we have attained by experiment.

10. This same subject may give rise to a multitude of questions; we will further examine the two following, less with a view of solving them than of indicating the number and the nature of the unknown elements on which their solution depends.

The first question is to ascertain whether there is, in the very

substance of the sun itself, a source destined to produce heat, to repair in some manner, by chemical, electrical or other actions, the losses of calorific rays which take place every instant; or whether, if these losses recurring incessantly without any reparation, there results, from century to century, a progressive diminution of temperature in which the globe of the earth must participate.

According to what we have just seen, each square centimetre of the sun loses in $1'$ a quantity of heat $v = 84888$ unities; in m number of minutes it loses $m\,v$; and the entire sun loses

$$4\,\pi\,R^2 . m\,v.$$

Now, if we suppose that the mass of the sun has a perfect conductibility for heat, so that its temperature is the same throughout,—if we represent its mean density by d and its mean capacity for heat by c, it is evident that, to be lowered 1°, the entire mass of the sun must lose a quantity of heat expressed by

$$\frac{4}{3} . R^3\,\pi\,d\,c,$$

since in m number of minutes it loses $4\,\pi\,R^2\,m\,v$; it follows that during this time it decreases by a number of degrees given by the relation

$$\frac{3\,v\,m}{R . d . c}.$$

The radius of the sun expressed in centimetres is 70 billions; the mean density d of the sun, as compared with water, is 1·4; it is deduced from the mean density of the earth 5·48, from the mass of the sun, which is 355 thousand times that of the earth, and from its volume, which is 1384 thousand times that of the earth.

Taking, moreover, for m the number of minutes which correspond to a year, namely 526000, and substituting for v its value 84888, this relation becomes

$$\frac{4}{3\,c}.$$

This is the number of degrees which the mass of the sun must cool each year, on the hypothesis of a perfect conductibility; if to this first hypothesis we add a second with relation to specific heat,—if, for example, we suppose that it is 133 times the specific heat of water, we find that the entire mass of the sun would then cool

$\frac{1}{100}$ of a degree per annum,
or 1 degree in a century,
or 100 degrees for 10 thousand years.

Thus the solution of the question before us now depends only on two elements which, without doubt, will remain for ever unknown to us, namely, the conductibility of the mass of the sun, and its capacity for heat; and we have just seen how, by means of these two elements, should we arrive at a knowledge of them, the question might be resolved in an exact manner. With regard to the hypotheses I have made respecting them, their only object is to show the extent of the uncertainties to which science is subjected on this point.

11. With the same object we shall proceed to examine another question, which however has the advantage over the preceding one of being more accessible to science, namely, whether the temperature of the sun may have some analogy with the temperatures which we are able to produce by chemical or electrical actions.

We shall see, in the following article, that the total quantity of heat emitted in 1′ by a square centimetre of surface is always expressed by

$$1{\cdot}146\,.f\,.a^t,$$

f being the emissive power of that surface, t its temperature, and a the number 1·0077 determined with great exactness by MM. Dulong and Petit.

We have found elsewhere that for the sun this quantity of heat is 84888. Then

$$\text{for } f = 1, \quad t = 1461,$$
$$\text{for } f = \tfrac{1}{10}, \quad t = 1761.$$

Thus the temperature of the sun depends on the law of radiation of heat and of the emissive power of the sun or of its atmosphere. In a former memoir* I have described an air pyrometer, by means of which I determined all the high temperatures up to the fusion of iron; I have since verified the fact that the law of radiation applies to temperatures which exceed 1000°; these experiments will soon enable me to ascertain whether the law in question extends in fact to temperatures of 1400° or 1500°; but we may even now regard such extension as very probable. With respect to the emissive power of the sun, it is unknown, but we cannot suppose it greater than unity. It follows therefore that the temperature of the sun is at least 1461°, that is to say nearly that of the melting point of iron, and that

* *Comptes Rendus de l'Académie des Sciences*, t. iii. p. 782.

this temperature might be 1761° if the emissive power of the sun were analogous to that of polished metals. These numbers do not differ much from those which I had determined by other principles and by other means of observation in my memoir of 1822.

12. Starting from the laws of cooling *in vacuo*, discovered by MM. Dulong and Petit, and developing a particular point of view which those able men of science had already indicated in their work, I was led to this general theorem.

The absolute quantity of heat e which is emitted in the unity of time by the unity of surface of any body, the temperature of which is $t + \theta$, and the emissive power of which is f, is always expressed by the relation

$$e = \mathrm{B} \cdot f \cdot a^{t+\theta},$$

B being an invariable constant, which depends solely on the zero of the scale and on the unities of time and of surface; its value is 1·146, taking the minute and the square centimetre for unities.

To demonstrate this general law of the emission of heat, let us consider a spherical body submitted to cooling or to the equilibrium of temperature in the centre of an inclosure also spherical; let us suppose that the body and the inclosure have, both of them, a maximum emissive power, in order to avoid the effects of reflexion; let us designate by e the quantity of heat which is emitted by the unity of surface of the inclosure, and let us suppose that the equilibrium of temperature is established; the total quantity of heat lost by the body in the unity of time is

$$e\,s,$$

s being the surface or $4\pi r^2$.

If we represent by e'' the portion of this heat which is received and absorbed by the unity of surface of the inclosure, we shall have

$$e''\,s'$$

for the total quantity of heat received by the inclosure, s' being its entire surface or $4\pi r'^2$.

Now the quantity lost by the body being equal to that which is received by the inclosure, we shall first have

$$e\,s = e''\,s',$$

whence

$$e'' = e \cdot \frac{s}{s'} = e \cdot \frac{r^2}{r'^2} = e \sin^2 \omega,$$

ω being the demi-angle at which the body is seen from a point of the inclosure.

If we now consider what the body receives from the inclosure, we easily perceive that it is a certain fraction b of the quantity of total heat e' which is emitted by each element, and consequently that it receives from the entire inclosure a quantity of heat expressed by

$$b\,e'\,s'.$$

Since the equilibrium is established, the quantity which the body receives is equal to the quantity which it loses, which gives

$$b\,e'\,s' = e\,s,$$

whence

$$b\,e' = e\,\frac{s}{s'} = e\,\frac{r^2}{r'^2} = e\,\sin^2\omega = e'';$$

that is to say, the entire body receives, from each element of the inclosure, a quantity of heat which is precisely equal to that which it imparts to it.

But at equilibrium, the temperatures of the body and of the inclosure being equal, the quantities e and e' must also be equal, because their emissive power is the same; therefore

$$b = \sin^2\omega.$$

Thus, whilst each element of the inclosure emits in all directions a certain quantity of heat e', the body receives from that element only

$$e'\sin^2\omega.$$

It is clear, moreover, that if, the temperature of the inclosure remaining constant, that of the body changes, the body will not less receive from the inclosure this quantity $e'\sin^2\omega$ which it received at equilibrium, e' being always the total quantity of heat emitted in all directions by the unity of surface of the inclosure.

Now if it be true that the absolute quantity of heat emitted in the unity of time by the unity of surface is expressed by a function of the form

$$e = \mathrm{B}f\,a^{t+\theta}$$

there results, for the total quantity $e\,s$ of heat lost by the body,

$$e\,s = s\,.\,\mathrm{B}\,.f\,a^{t+\theta};$$

at the same time, the inclosure having the same emissive power f and the temperature θ, we shall thus have

$$e' = \mathrm{B}\,.f\,a^{\theta},$$

and for the total quantity of heat emitted by the inclosure,

$$s' e' = s' . \mathrm{B} . f a^{\theta}.$$

As the body receives only a portion, $\sin^2 \omega$, of this heat, its real and definitive loss will therefore be

$$s e - s' e' \sin^2 \omega = s \mathrm{B} f . a^{t+\theta} - s' \sin^2 \omega . \mathrm{B} . f a^{\theta},$$

or on account of $s' \sin^2 \omega = s$,

$$s . \mathrm{B} . f (a^{t+\theta} - a^{\theta}).$$

Such is the quantity of heat lost by the body.

If now we represent its weight by p and its specific heat by c, it is evident that for one unity of heat which it loses, its temperature is only lowered a number of degrees denoted by

$$\frac{1}{cp}.$$

Consequently, whilst it loses a number of unities of heat expressed by

$$s \mathrm{B} . f (a^{t+\theta} - a^{\theta}),$$

it loses in temperature only a number of degrees denoted by

$$\frac{s . \mathrm{B} . f}{cp} (a^{t+\theta} - a^{\theta}):$$

this is, properly speaking, its velocity of cooling.

To make this formula coincide with that of MM. Dulong and Petit, it is sufficient to suppose

$$m = \frac{s . \mathrm{B} . f}{cp},$$

and it would moreover be necessary that the constant should be null, if it had been added to the value of e, as is easy to be seen, supposing the body only to be polished; this demonstrates the exactness of the general relation

$$e = \mathrm{B} f a^{t+\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

and it shows, at the same time, the elementary composition of the coefficient m, the numerical value of which has been given by the experiments of cooling; thus the magnitude of this coefficient is in direct ratio to the surface of the body and its radiating power, and in inverse ratio to the mass of the body and its capacity for heat.

With respect to the value of the constant B, it may be deduced from the preceding relation, at least very approximately,

since the coefficient m has been determined with great care by MM. Dulong and Petit, and found equal to 2·037 for a thermometer with glazed surface which was spherical, filled with mercury, and which was 6 centimetres in diameter.

Assuming therefore

$$m = 2{\cdot}037,$$
$$c = 0{\cdot}033,$$
$$\frac{s}{p} = \frac{1}{13{\cdot}65},$$
$$f = 0{\cdot}8,$$

we find $\mathrm{B} = 1{\cdot}146.$

This result cannot be perfectly exact, both because the value of f is a little hypothetical, and because the true dimensions of the thermometer in question being wholly useless for the researches on cooling, MM. Dulong and Petit have only indicated them in a general manner: it is however certain that the error cannot be considerable, and we shall adopt the value of B as sufficiently near*.

13. We may, indeed, demonstrate directly, in another way, that the values of the coefficient m are undoubtedly in a direct ratio to the surface and the emissive power of the bodies subjected to cooling, and in an inverse ratio to the weight of these bodies and their capacity for heat.

In fact, admitting that the velocity of cooling in absolute cold is expressed as in the formula of MM. Dulong and Petit, by the relation

$$v = m\,a^t,$$

we obtain by integration the following formula:

$$x = \frac{1}{m\,l'\,a}\left(\frac{a^{\mathrm{T}-t}-1}{a^{\mathrm{T}}}\right), \quad \ldots \quad (3.)$$

in which T represents the initial temperature of the body, and x the number of minutes which elapse whilst the body falls from the initial temperature T to any temperature t.

Consequently, for the body to be lowered 1° is required a time expressed by

$$x = \frac{1}{m\,l'\,a}(a-1)\,a^{-\mathrm{T}}.$$

Now, if we represent the surface of the body by s, its weight by p, and its specific heat by c, it is evident that in falling 1° it

* See Note 1, p. 85.

loses a quantity of heat $p\,c$, and as it loses it by one surface s, each unity of surface loses

$$\frac{p\,c}{s};$$

but since the body requires a time x to fall 1°, it follows that in a time 1 it falls

$$\frac{1^\circ}{x}.$$

Thus in the unity of time, the unity of surface loses a quantity of heat expressed by

$$\frac{p\,c}{s}\cdot\frac{m\,l'\,a}{a-1}\cdot a^{\mathrm{T}}.$$

For another body which should have the same initial temperature T, the loss would be

$$\frac{p'\,c'}{s'}\cdot m'\cdot\frac{l'\,a}{a-1}\,a^{\mathrm{T}}.$$

As these losses must be proportional to the radiating powers f and f' of the two bodies, we should have

$$\frac{m}{m'}=\frac{s\,.\,f\,.\,p'\,c'}{s'\,.\,f'\,.\,p\,c},$$

that is to say, the coefficients m and m' are in fact in a direct ratio to the surfaces and the radiating powers, and in an inverse ratio to the masses and the capacities.

14. The formulæ (2) and (3) contain the laws of cooling in absolute cold; they may be employed to solve a great number of questions.

The first shows, for example, that under the equator, where the temperature of the earth is on an average 30°, each square centimetre loses in unities of heat,

1·44 in 1′,
1037·00 in 12 hours;

whence it follows, that in a column of water 10 metres in depth, there would in twelve hours be only a lowering of 1°, if by its upper surface that column lost its heat in absolute cold without receiving compensation for what it loses, either by its free surface or by its sides.

The second shows that in absolute cold the thermometer of MM. Dulong and Petit would take

34′·14 to fall from 100° to 0,
74′·66 to fall from 0 to −100°;

but this small globe was only 6 centimetres in diameter, and if we make the same calculations for a similar body having, for example, the dimensions of the earth, we find that in absolute cold this globe would take

13,640 years to fall from 100° to 0,
29,830 years to fall from 0 to −100°.

These examples may show that there has perhaps been some exaggeration in the ideas which have been hitherto entertained of absolute cold and the phænomena which would be manifested on the surface of the earth if the temperature of space were excessively reduced below the zero of our thermometers; they show at the same time that the essential laws of heat are established upon such fixed principles that sudden changes of temperature are not less impossible in the system of the world than the sudden changes resulting from mechanical actions.

15. The theorem relative to the emission of heat enables us to determine the conditions of equilibrium of temperature of the atmosphere; for this purpose we shall proceed to consider in a general manner the conditions of equilibrium of temperature of a globe protected by any diathermanous covering and suspended with its envelope in the middle of a spherical inclosure.

Let us designate by s, s'', s' the surfaces of the globe, of the envelope, and of the inclosure; by e, e'', e' the quantities of heat emitted in the unity of time by each of the unities of surface of s, s'', s'; we designate by b the absorbing power which the diathermanous envelope exerts upon the heat emitted by the globe, and by b' the absorbing power which it exerts upon the heat emitted by the inclosure.

The globe emits in the unity of time a quantity of heat $e\,s$; one portion $b\,e\,s$ is absorbed by the envelope, and one portion $(1-b)\,e\,s$ traverses the envelope to reach the inclosure.

The inclosure emits a total quantity of heat $e'\,s'$; one part $e'\,s'\sin^2\omega$ falls upon the diathermanous envelope, designating by ω the demi-angle at which the inclosure is placed with regard to the envelope; this latter absorbs a portion of it, $e'\,s'\,b'\sin^2\omega$, and it lets pass a portion, $e'\,s'\,(1-b')\sin^2\omega$.

The envelope emits a quantity of heat $e''\,s''$ toward the globe, and an equal quantity of heat $e''\,s''$ toward the inclosure.

The sum of the quantities of heat which the envelope loses is

equal to the sum of the quantities of heat which it receives, and this gives a first equation,

$$2\,e''\,s'' = b\,e\,s + b'\,e'\,s'\,\sin^2\omega.$$

We obtain in the same manner for the globe and for the inclosure, two other equations which result from the equality between the quantities of heat received and lost, namely,

$$e\,s = e''\,s'' + (1-b')\,e'\,s'\,\sin^2\omega,$$
$$e'\,s'\,\sin^2\omega = e''\,s'' + (1-b)\,e\,s.$$

It is easy to see that these three equations are reducible to two, because the first is a consequence of the two last, and might be deduced from them.

If we now suppose the radius of the envelope to be sensibly equal to the radius of the globe, as is nearly the case with the atmosphere around the earth, the equations become

$$e = e'' + (1-b')\,e',$$
$$e' = e'' + (1-b)\,e,$$

and this leads to the three following relations:

$$\frac{e}{e'} = \frac{2-b'}{2-b},$$
$$\frac{e}{e''} = \frac{2-b'}{b+b'-b\,b'},$$
$$\frac{e'}{e''} = \frac{2-b}{b+b'-b\,b'}.$$

If, now, we designate by t, t'', t' the temperatures of the globe, of the envelope and of the inclosure; by f, f'', f' their emissive powers, we shall have, in virtue of the principle above established, the three other equations:

$$e = \mathrm{B}\,.\,a^t,$$
$$e' = \mathrm{B}\,.\,a^{t'},$$
$$e'' = \mathrm{B}\,.\,f''\,a^{t''},$$

on the supposition we have made, to simplify the matter, that the globe and the inclosure have maximum emissive powers.

These equations, combined with the preceding ones, give—

$$a^{t-t'} = \frac{2-b'}{2-b},$$
$$a^{t-t''} = f''\,.\,\frac{2-b'}{b+b'-b\,b'},$$
$$a^{t'-t''} = f''\,\frac{2-b}{b+b'-b\,b'}.$$

Such are the general relations which give in all possible cases the differences of temperature required by the conditions of equilibrium between the globe and the inclosure, the globe and the envelope, the inclosure and the envelope. We see that these differences depend essentially upon the relative values of b and of b', that is to say, on the absorbing powers which the diathermanous envelope exercises upon the heat of the globe and upon that of the inclosure.

If we first suppose that these absorbing powers are equal, that is to say that $b = b'$, it results that

$$t = t',$$
$$a^{t-t''} = \frac{f''}{b},$$
$$a^{t'-t''} = \frac{f''}{b}.$$

Thus all diathermanous envelopes which exert equal absorbing powers on the rays of heat of the globe and the inclosure, do not prevent the globe and the inclosure having for the equilibrium exactly the same temperature as if the diathermanous inclosure did not exist, and *vice versâ*.

With regard to the temperature of the diathermanous envelope itself, we see that it can only be equal to that of the globe and of the inclosure, under the condition that $f'' = b$, that is to say, that the emissive power of that envelope is equal to its absorbing power, which, in fact, is the case with rock-salt and air, as I have ascertained by experiment.

But when these conditions are not fulfilled, when the diathermanous envelope exerts unequal absorbing powers on the heat of the inclosure and on that of the globe, the principle of the equality of temperature ceases to be true, and immediately there are then manifested, contrary to the ordinary laws of equilibrium, differences more or less considerable between the temperatures of the globe, the inclosure and the envelope. The following table contains some of the results which are obtained in discussing the formulæ, after having attributed different values to b' and to b.

Values		Excess of temperature		
of b'.	of b.	of the globe over the inclosure $t-t'$.	of the globe over the envelope $t-t''$.	of the inclosure over the envelope $t'-t''$.
0·3	0·7	35·0	53·5	18·5
0·3	0·8	45·5	59·5	14·0
0·3	0·9	57·0	65·0	8·0
0·4	0·8	38·0	49·0	11·0
0·4	0·9	49·0	56·0	7·0
0·5	0·9	41·0	46·0	5·0
0·5	0·95	46·5	49·5	3·0
0·0	0·9	78·0	91·0	13·0
0·0	0·1	91·0	91·0	0·0

It results, for example, that if the diathermanous envelope absorbs only three-tenths of the heat of the inclosure and eight-tenths of that of the globe, the temperature of the globe then exceeds that of the inclosure by 45°·5, and that of the envelope by 59°·5, which last is thus 14° below the temperature of the inclosure itself.

There is, however, a limit to the accumulation of heat upon the globe and to the cooling of the envelope, and that limit is 91°.

This effect of diathermanous envelopes is very remarkable, and it becomes perhaps still more striking when we ascend to the temperatures themselves instead of stopping at their simple difference, since the preceding examples then lead to this result, that if an inclosure has its sides kept throughout at the temperature of melting ice, a globe suspended in the centre of this inclosure, having no other heat but what it receives from it, may nevertheless, under certain conditions, be raised to the temperature of 40° to 50° above zero, that is to say, to a temperature considerably higher than that of the torrid zone, and maintain this excess of temperature without ever cooling, on condition of no longer being in equilibrium of temperature, and consequently of being instantly heated again by the rays of the heat of the inclosure. For this phænomenon, it is sufficient for the globe to be protected by a diathermanous envelope, possessing the double property of absorbing only half the heat emitted by the surface of the inclosure, and of absorbing on the contrary about nine-tenths of the heat emitted by the surface of the globe.

Lastly, to complete this consequence, with relation to the envelope itself, which is the sole cause of this effect, we must also add, that this envelope included between an inclosure at zero

and a globe at 45° or 50° would be found to have only a mean temperature lower by some degrees than zero, its lower strata being warmer than the inclosure, and its upper strata much colder, following a certain law of decrease which may be calculated when the proper data are obtained.

Our present remarks (supposing the inclosure to be at the temperature of melting ice, or rather supposing that the heat which reaches the globe is uniformly distributed and equivalent in quantity to that which would proceed from such an inclosure possessing a maximum emissive power) apply, under the same conditions, to an inclosure of any temperature, provided that this temperature does not vary from the degrees of heat or cold to which the law of cooling may extend.

Such, in general, are the effects produced by diathermanous envelopes from the inequality of the absorbing actions which they may exercise upon the different rays of heat which traverse them; with respect to the cause of these unequal absorptions, Delaroche has demonstrated, on one side, that it depends on the sources of heat themselves, and consequently on the peculiar nature of the calorific rays; and M. Melloni has shown, on the other hand, that it depends also, under certain relations, on the nature of the diathermanous substances.

16. Hitherto it has been admitted that two athermanous surfaces of the same temperature emit identical rays of heat, or at least rays of heat which experience always equal absorptions in traversing the same media; but it is perhaps not impossible to arrive at the discovery, in this respect, of some differences which depend either upon the diversity of the emissive powers, or on the very nature of the bodies.

This is an essential point, to which the researches of M. Melloni have, without doubt, not failed to call the attention of natural philosophers. If these rays, emanating from sources of equal temperature, resist all tests, if they preserve their identity in traversing the same diathermanous media, it will be impossible to obtain, in the experiments of the laboratory, any accumulation of heat by the interposition of diathermanous envelopes; since in that case the absorbing powers of these envelopes would necessarily be the same upon the rays of the inclosure and on those of the globe or of the interior thermometer.

This impossibility, however, could not affect the consequences which we shall proceed to deduce from the formulæ with rela-

tion to the effects which the atmosphere produces either upon the heat of the sun, or upon the heat of the other heavenly bodies, which is in general designated under the name of *heat of space*, or *planetary heat*.

With regard to the solar heat no doubt exists: we know that in traversing diathermanous substances it is less absorbed than the heat which is derived from different terrestrial sources, the temperature of which is not very high. It is true that we have been able to make the experiment only upon solid or liquid diathermanous screens; but we regard it as certain that the atmospheric stratum acts in the manner of screens of this kind, and that consequently it exercises a greater absorption upon the terrestrial than upon the solar rays; we must also add, that this difference of action does not result, as is sometimes said, from the solar heat being luminous and the terrestrial heat obscure; for, up to the present day, all that is known with regard to this subject leads us to think that there is neither warm light nor luminous heat: the rays of heat and of light may derive their origin from the same source, be emitted at the same time, and coexist in the same pencil of rays, but they preserve a distinctive character, since, on the one hand, they may be separated the one from the other, and on the other hand, there is no instance of a ray of heat which has been transformed into a ray of light, nor of a ray of light, properly speaking, which has been transformed into a ray of heat. The inequality of absorption in question depends therefore on peculiar properties which the rays of heat assume when they are emitted by sources at a temperature more or less high, and these properties are only maintained, or perhaps developed more, when the temperature of the sources is sufficiently raised for them to emit, like the sun, light at the same time as heat.

With respect to the heat of space, there is another distinction to be made: it must be considered in relation to its quantity and in relation to its nature.

Considered in relation to its quantity, it is measured, as all other heat, by the effects which it produces; that is to say by the quantity of ice which it can melt, or by the elevation of temperature which it would impart to a given quantity of water. It is upon this principle that M. Fourier has first shown that it was necessary to take account of the heat of space in order to explain the phænomena of the terrestrial temperatures; and it

is upon this principle also that he has indicated, in a general manner, that the temperature of space ought to be very little inferior to the temperature of the poles of the earth, and about 50° or 60° below zero; expressing by this valuation nothing else than that the total heat which reaches the earth from all the celestial bodies, excepting the sun, is equivalent in quantity to that which would be emitted on the globe of the earth by an inclosure at a maximum emissive power, the sides of which should be kept at the temperature of 50° or 60° below that of melting ice. The essential point in this manner of regarding the phænomena is the possibility of substituting for the whole of the celestial bodies a fictitious inclosure, or an athermanous surface kept throughout at a certain temperature; it remains to examine whether there are experiments by which this temperature itself can be determined, and with what degree of approximation we may hope to obtain it.

Considered in relation to its nature, the heat of space gives rise to a multitude of questions which it would be useless to treat of here; we shall limit ourselves therefore to some observations inherent to our subject. We remark, first, that if the fictitious inclosure which has just been spoken of can, when a proper temperature is assigned to it, represent strictly, or very nearly, the heat of space, it can only represent it for its quantity; and it will never represent it for its nature, since the heat of space possesses essentially properties due to its origin, which it could not derive, without doubt, from a source the temperature of which should be lower than melting ice. We instantly see that from this there result conditions which it is impossible for us to reproduce in our experiments, namely, a heat which is by its quantity as if it emanated from a cold source, and by its nature as if it emanated from a hot source. To explain this kind of contradiction it suffices to admit that any line, starting from the earth and prolonged indefinitely in space, will not essentially encounter a body which can transmit heat to the earth; or, in other words, it is sufficient to admit that the planetary inclosure, in reality, is not for us an inclosure becoming continuous by the assemblage of numberless bodies which are dispersed in the depths of space at distances continually increasing; then, in fact, there will be points or small portions of the celestial vault which would transmit heat to us, and other portions doubtless

larger which would not transmit heat to us, because the corresponding lines are prolonged indefinitely in space.

We thus understand that the heat of space may be assimilated to the solar heat in its nature and origin, if not in its quantity, and that the atmosphere consequently exerts upon it the same absorption. This being established, the general conditions of equilibrium of the diathermanous envelopes which we have discussed above find here their direct application: it is sufficient to admit that the globe which we have supposed of any given dimensions, is the globe of the earth; that the inclosure is that which represents the unknown temperature of space; and, lastly, that the diathermanous envelope is nothing else than the atmosphere supposed at first without clouds, and possessing the property of absorbing only in the perpendicular direction about 20 or 25 hundredth parts of incident heat, as we have found by the experiments on the solar heat related above. As the absorbing action which the atmosphere exerts upon the rays emitted by the earth is necessarily greater, it results that all the consequences at which we have arrived apply to the equilibrium of the terrestrial temperatures.

In consequence, the phænomena which occur without the action of the sun and without the effects of the interior heat of the globe are the following:—

1. The temperature of the surface of the earth is considerably higher than the temperature of space:

2. The mean temperature of the atmosphere is necessarily lower than the temperature of space, and still more than the temperature of the earth itself:

3. The decrease of the temperature in the atmosphere is not at all due to the periodical action of the sun, nor to the ascending and descending currents which that action may determine near the surface of the earth; it will even take place when the sun would not heat either the earth or the atmosphere, because it is one of the conditions of equilibrium of diathermanous envelopes, and its real cause lies in the unequal absorbing actions which the atmosphere exerts upon the rays of heat derived from space, and upon those which are emitted all round the globe by the surface of the soil or by that of the seas.

M. Fourier is, I think, the first who has had the idea of regarding the unequal absorption of the atmosphere as exercising

an influence on the temperatures of the soil. He had been led to this by the beautiful experiments made by De Saussure, in 1774, on some elevated summits of the Alps and in the adjacent plains, with a view to compare the relative intensities of solar heat. On that occasion * M. Fourier states in a precise manner one of the principles which have served me to establish the equations of equilibrium; only that he appeared to apply it merely to the solar action, supposing that this periodical action is the principal cause of the decrease of temperature of the atmosphere.

On another side, M. Poisson, in his last work, has already shown that the upper strata of the atmosphere must necessarily be at a much lower temperature than the temperature of space: he has deduced this result, on one hand, from the numbers at which he has arrived to express the temperature of space, and on the other, from the mechanical conditions of equilibrium, which could not be fulfilled at the limits of the atmosphere if the air did not there experience a degree of cold sufficient to make it lose all its elasticity. This consequence, which might appear extraordinary when presented only as a mechanical necessity, may perhaps now appear, if not more certain, at least more natural, since it results also from the laws of radiant heat, and since it is by this explained and referred to its real origin.

17. If we now return to the conditions of equilibrium of diathermanous envelopes to examine the causes which may have influence upon their double absorbing power, we shall remark that the specific heat of the substance of these envelopes cannot change without the absorbing powers changing also in a certain relation. In fact, if around the globe we substitute for a given envelope another envelope of the same mass and the same matter, which differs from it only in its capacity for heat, it is extremely probable that the effects will be different, that these two envelopes will not take the same temperature, and that they will not determine equal accumulations of heat on the globe, even supposing that the relative values of the two absorbing powers remain the same in each of them.

This simple remark, joined to some other considerations which cannot be developed here, has led me to admit that the absorbing powers of the same elastic fluid, considered as a diathermanous substance, are proportional to its mass and to its capacity for

* *Annales de Chimie*, tome xxvii. p. 155.

heat. Thus, in dividing the atmosphere, for example, into 100 concentric strata of the same mass, the individual absorbing powers of any two strata will be proportional to the different specific heat of these two strata. Near the surface of the earth, where the pressure is great and the capacity small, the proportion of heat absorbed will be consequently less than near the limits of the atmosphere, where the pressure is feeble and the capacity considerable; we see that at the same time the inferior stratum occupies a vertical height much smaller than that of the upper stratum. This consideration modifies, as we have stated, the quantities of solar heat which reach the summits of the high mountains, and it leads to a general expression for these quantities of heat, in which it remains to substitute the barometric pressures and the corresponding specific heats. It is thus that the absorption, which we have found and verified by experiment, may extend to the different heights to which it is possible to ascend in order to make observations there analogous to those which we have made at Paris.

Lastly, this same principle, and those which have been developed above, lead us to express, in a simple manner, the total quantity of radiant heat which is emitted in a given time by the unity of surface of any atmospheric strata whatever. This quantity of heat depends, in fact, only on the peculiar temperature of that stratum which we shall represent by t, on its capacity for heat c, and on its mass m, then on the number $B = 1{\cdot}146$, which is the constant of the radiation; and lastly, on an unknown constant k which depends on the nature of the elastic fluid; it value is then

$$B\,k\,m\,c\,a^{t}.$$

For another stratum of the same mass, situated at a greater height, the temperature of which would be t' and its capacity c', the total quantity of heat lost in the same time would be

$$B\,k\,m\,c'\,a^{t'}.$$

This being established, let us consider the state of the atmosphere under the equator, admitting that the sky there has been long unclouded, and that the equilibrium of temperature is there established throughout the height of the atmospheric column: then, the mean temperature of each day being nearly constant upon the soil, and constant also in each of the strata of air, at whatever height, the soil and the different strata of the atmo-

sphere must lose every day all the heat that they receive. Now the quantity of heat received by one of the lower strata, for example, depends upon the absorbing power which is peculiar to it, and on the incident heat which reaches it, both from the earth below, and also from the sun and from space above. It is the same with respect to one of the upper strata: only it is evident that this will receive from the sun and from space much more incident heat than the lower stratum, since this heat is weakened more and more in proportion as it penetrates into deeper strata; it is also evident that the lower stratum in turn will receive in compensation much more terrestrial heat than the upper stratum, because the terrestrial heat is weakened by the same cause in proportion as it penetrates into more elevated strata. The relation of these received quantities, or rather of the quantities received and absorbed by any two strata, may be calculated approximately, and we find that it does not vary much from unity, provided at least that we do not arrive at strata very near the limits of the atmosphere: if we assume it equal to unity, this signifies that two strata of air, one upper and the other lower, very near to or very distant from one another, absorb each day equal quantities of heat; but since they both lose all that they receive, it results very evidently that they lose in the same time equal quantities of heat. Thus, we should have

$$\mathrm{B}\, k\, m\, c\, a^{t} = \mathrm{B}\, k\, m\, c'\, a^{t'},$$

whence

$$t - t' = \frac{1}{l\, a} . l . \frac{c'}{c}.$$

This result, which expresses in so simple a manner the law of the decrease of the temperature of the air for the equatorial region, and which seems to extend nearly to the limits of the atmosphere, requires to be verified by experiment, as much at least as these verifications are possible.

Now we know, by the researches of M. de Laplace and M. Poisson, that the capacities of elastic fluids for heat are connected with the pressures which these fluids support by a relation of the form

$$\frac{c'}{c} = \left(\frac{p}{p'}\right)^{1 - \frac{1}{k}},$$

which becomes for dry air

$$\frac{c'}{c} = \left(\frac{p}{p'}\right)^{\frac{3}{11}},$$

and we equally know that this formula has been verified by very accurate experiments of MM. Gay-Lussac and Welter, which extend for the pressures from 1460 mill. to 144 mill., and for the temperatures from 40° above zero to 20° below.

Thus we may already calculate the capacities of the different strata of air up to four-fifths of the height of the atmosphere: it would be, however, interesting to continue the experiments of M. Gay-Lussac, and to extend them, if it be possible, preserving the same precision, down to temperatures of 60° or 80° below zero, —a temperature which we can now obtain by means of the apparatus of M. Thilorier*.

However, if we admit provisionally that the formula of M. Poisson actually extends to a pressure of $\frac{1}{100}$ of atmosphere, we find that the temperature of the corresponding stratum at that pressure would be lower by 163° than the mean temperature of the stratum nearest the soil, and, as the latter is 27° above zero, the other would be 136° below zero.

Calculating the temperatures of the 100 strata corresponding to each of the 100ths of the atmospheric pressure, and taking the mean of them, we obtain approximately what we may call the mean temperature of the atmospheric column, because it is in fact in virtue of this temperature that the entire column emits radiant heat: the calculation gives for this mean − 8°.

There is still another verification possible. We know that the barometric formula is exact up to a considerable height, and that it establishes a relation between the vertical distance of the two strata and the corresponding pressures. This relation is approximately

$$z = 18393 \,.\, l.\left(\frac{p}{p'}\right);$$

on combining it with the preceding, we arrive at this result—

$$t - t' = \frac{z}{224{\cdot}8},$$

that is to say, that the difference of the temperatures of two strata is 1° for every 225 metres within the extent to which the barometric formula can be applied.

We know that the experiments of M. de Humboldt give 200^{m}; this difference of one-eighth depends doubtless on many causes, and particularly on the fact that the formula which connects the capacities with the pressures can only be employed for dry air,

* See my experiments on this subject, *Comptes Rendus*, t. iv. p. 513.

whilst the air is in general very humid under the equator, on account even of its temperature.

18. A thermometer which is exposed on the ground to the nocturnal radiation receives heat from two different sources, namely from space and from the atmosphere. The heat of space being submitted to absorption like the solar heat during its atmospheric passage, only three- or four-tenths of it can in general reach the thermometer, at least supposing that the experiments are not made on high mountains. With respect to the heat emitted by the atmosphere itself in the course of the night, it is the effect of the individual radiation of all the concentric strata which we can imagine from the level of the sea up to the limits of the atmosphere, and it depends consequently on the distribution of the temperatures throughout the whole height of the atmospheric column; we may add, that its influence is much more considerable than has hitherto been supposed. For the rest, whatever be the relation of the intensities of these two causes, it is evident that we may conceive a single cause capable of producing an effect equal to that which results from their simultaneous action; or, in other terms, we may suppress in thought the heat of space and that of the atmosphere, and conceive an inclosure, of a maximum emissive power, the temperature of which is such that it imparts to the thermometer and to the ground precisely as much heat as they receive at once from the atmosphere and from space; this is the unknown temperature of that *zenithal inclosure* which I term the *zenithal temperature.*

The object of this manner of viewing the phænomena is not to represent the peculiar and perhaps unequal actions which the thermometer experiences in such or such a direction, but only to represent with exactness the definitive and total action to which it is submitted, so that its depression below the ambient temperature is the same with the zenithal inclosure as with the atmosphere and space united. It is under this condition that we are now permitted to assign to the zenithal inclosure a uniform temperature in all the portions of its extent. In short, it is evident that the zenithal temperature is necessarily variable at each instant for the same point of the surface of the earth, and still more variable for one point than another, because it is composed of a fixed element, which is the temperature of space, and of an element incessantly changing, which is the temperature of the different atmospheric strata.

The advantage there may be in resolving thus the problem will be better comprehended when we shall have shown the new relations which thence result between the unknown quantities which we seek to determine. Let us represent by z the zenithal temperature and preserve the same designation for the other quantities, namely,—

t' for the temperature of space;

t'' for the mean temperature of the atmospheric column;

b for the absorbing power which the atmosphere exerts upon the terrestrial heat; and

b' for the absorbing power which the atmosphere exerts upon the celestial heat.

This being established, let us consider,—

1. That during the unity of time the zenithal inclosure emits by the unity of surface a quantity of heat,

$$\mathrm{B}\,a^{z};$$

B being the same constant 1·146 of which we have previously spoken; there is no coefficient relative to the radiating power, because we must suppose it equal to unity.

2. That the atmosphere emits likewise a quantity of heat

$$\mathrm{B}\,b\,a^{t''},$$

because its emissive power is equal to its absorbing power, which we have represented by b.

3. Lastly, that space emits a quantity of heat

$$\mathrm{B}\,a^{t'},$$

but that there is only one portion of it $(1-b')$ which directly traverses the atmosphere to reach the ground, whence it follows that with relation to the thermometer which rests upon the ground, it is as if space had an emissive power $1-b'$, and as if it transmitted only a quantity of heat

$$(1-b')\,\mathrm{B}\,a^{t'}.$$

Since the zenithal inclosure replaces the atmosphere and space, the quantity of heat which it emits with relation to the thermometer must be exactly equal to the sum of the quantities of heat emitted by the atmosphere and space.

We have then

$$\mathrm{B}\,a^{z} = \mathrm{B}\,b\,a^{t''} + (1-b')\,\mathrm{B}\,a^{t'},$$

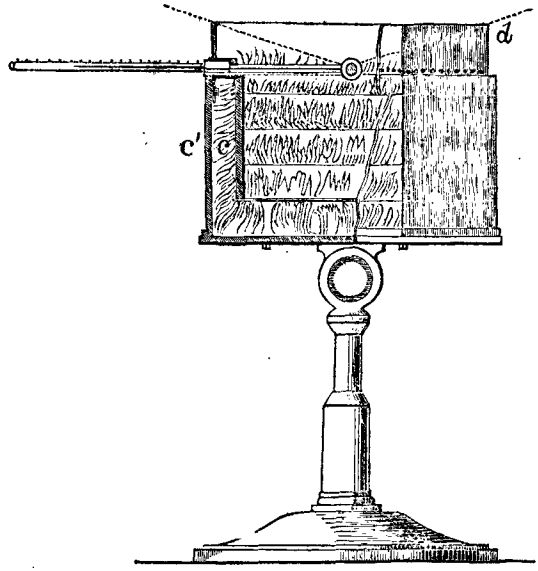
$$a^{z} = b\,a^{t''} + (1-b')\,a^{t'}. \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

Such is the general relation which connects incessantly the zenithal temperature with the temperature of space, with the mean

and variable temperature of the column of air, and with the two unequal absorbing powers of the atmosphere.

19. Let us now attempt to indicate how it is possible to observe the zenithal temperature each instant of the night, nearly as we observe the temperature of the air.

I have employed two methods for this purpose: one which rests on the employment of mirrors, and the other on the employment of a novel instrument which I call *actinometer*; we know that this name is already applied to a very important invention of Sir J. Herschel, and it seems to me happily chosen by that illustrious astronomer to designate all kinds of apparatus the object of which is to measure the effects of radiation, whatever be the principle of their construction.



It will be sufficient to indicate here the second method: I shall only remark with regard to the first, that the cooling which is observed at the focus of a mirror whose axis is directed towards the zenith, does not depend upon the concentration of the rays, as has been hitherto supposed; a simple plate of polished metal, or rather an expanded cone, produces nearly the same effect, so that I have found it possible to substitute for the mirrors reflectors of this kind which are much more convenient. However, with the reflectors, as with the mirrors, the experiments are delicate and the formulæ very complicated; they con-

tain the real temperature of the air, and the relation of the cooling resulting from its contact to that resulting from the radiation—two data upon which it is impossible not to have some uncertainty.

The actinometer is represented in the above figure: it is composed of four rings of two decimetres diameter, furnished with swans'-down, and resting one upon another, so that the down may not experience any compression: the swans' skin itself forms the foundation of the circle of each of these rings. This system is inclosed in a first cylinder of silver plate c, enveloped also in swans' skin, and contained in a larger cylinder c'. A thermometer rests on the centre of the upper down: the margin d is of such a height that the thermometer can only face two-thirds of the hemisphere of the sky; this margin is perforated with holes at the level of the down, in order that the cold air may flow regularly *.

This apparatus is during the night exposed to the radiation of the sky, and its thermometer and an adjoining thermometer freely suspended in the air at four feet from the ground are observed hourly; the zenithal temperature is deduced from the difference of these temperatures, or from the lowering of the actinometer; but for this the apparatus must have received a graduation, which we proceed to indicate.

20. If the actinometer had an indefinite surface, and were maintained at a constant temperature *in vacuo* under an hemispherical inclosure, it would evidently take the temperature of the inclosure; on the contrary, with its real form, facing only two-thirds of the hemisphere, and enveloped in a stratum of air which warms it again, it must always remain at a higher temperature than that of the inclosure. The graduation is intended to determine how much it is heated, so that it is sufficient to know its temperature and that of the ambient air to deduce thence the temperature of the inclosure, with which it is in interchange of radiant heat. It is obvious that there must exist a simple relation between the temperature of the inclosure and the lowering of the actinometer. To discover this relation, I composed an artificial sky with a zinc vessel a metre in diameter, supported at a height of two metres by three slender columns; this vessel, the bottom of which was blackened, was filled with a refrigerating mixture at $-20°$, and the actinometer was placed vertically beneath at such distances that the central

* See Note 2, p. 89.

thermometer faced successively extents corresponding to one quarter hemisphere, one-third hemisphere, and two-thirds hemisphere; in each position I awaited the equilibrium of temperature, and noted at the same time the temperature of the ambient air and that of the apparatus. Analogous experiments, repeated at the temperature of melting ice and at other intermediate temperatures, have led me to the following result:— If from the ambient temperature nine-fourths of the lowering of the actinometer be taken away, we always find the temperature of the artificial sky. This result evidently applies to the celestial vault, or rather to the zenithal inclosure; consequently, if we observe during the night the temperature t of the ambient air, and the lowering d of the actinometer, we shall thence deduce the zenithal temperature by the formula

$$z = t - 9\frac{d}{4},$$

which is the result of the graduation.

21. Further on will be found a table containing some of the series of experiments which have been made during very beautiful nights, and in calm weather, to determine the zenithal temperature. These experiments confirm the fact that the zenithal temperature is lowered during the night, nearly as the temperature of the ambient air; this progressive lowering, from the setting to the rising of the sun, is an essential fact which leads immediately to an important consequence.

In fact, we have seen that the zenithal temperature is expressed by the sum of two terms; one depending on the mean temperature of the atmospheric column, which is variable, and the other depending on the temperature of space, which is fixed. Now since the zenithal temperature experiences, in a single night, considerable variations, this is an evident proof that the fixed term which enters into its expression has only a very small value with relation to the variable term, and consequently that, in the nocturnal radiation, the heat of space is very small in relation to the heat which is derived from the radiation of the atmosphere.

This consequence can scarcely be reconciled with the opinions which attribute to space a temperature the value of which would not be lowered beneath zero a very great number of degrees; but it is perfectly reconcileable with the known facts which already might have furnished indications in this direction, had they all been analysed with the attention which they merit.

The numerous results of Mr. Wells, of Mr. Daniell, and of all the other natural philosophers who have made experiments on nocturnal radiation, not only prove that a thermometer exposed on the ground during the night, in an open place, is cooled 6°, 7°, or even 8° below the ambient temperature; they also prove that this phænomenon is reproduced, almost with the same intensity, in the coldest months of the year, that is to say in January and February, when the temperature of the air has fallen many degrees below zero. Thus Wilson observed a difference of nearly 9° between the temperature of the air and that of the surface of the snow; Scoresby and Captain Parry have observed analogous depressions in the Polar regions, when the temperature of the air was more than 20° below zero.

If we now consider that the heating power which the stratum of air exerts by its contact with the thermometer of the ground, which is colder than it, is nearly the same, whether it be at 10° above zero or 10° below, it results that the cooling power which maintains this thermometer at −18° in the second case, has also the same energy as the cooling power which maintains it at +2° in the first case; and, as this cooling power depends on the temperature of space, it follows also that the temperature of space is much lower than −18°; for if it were only −30° or −40°, the thermometer which is at −18° whilst the air is at −10° would be too near for the heat of space to be able to keep it at the same depression below the air as the thermometer which is at +2° whilst the air is at 10°. What has perhaps hitherto prevented our arriving at this conclusion, is that in the explanations which have been given of the nocturnal radiation, a peculiar cooling power has been generally attributed to the upper strata of the atmosphere, which are known to be very cold, forgetting in some measure that, cold as they are, it is nevertheless heat which they transmit, and that this heat is added to that of space to augment its effects.

The results which I have obtained by means of the actinometer are therefore in accordance with all known facts; it was perhaps essential to make this remark, in order to show that, if the consequences at which we shall arrive are in some points contrary to received opinions, this results from the nature of things rather than from the inaccuracy of the experiments.

22. Considering the equation (4.) as an equation of condition, which must always be satisfied for every value of the zenithal temperature given by experiment, I have been able to determine

the limits for the temperature of space; but the phænomena which are manifested in the equatorial regions, and which there prevail in a constant manner throughout the year, lead to another fundamental equation, from which we may derive the temperature of space without having recourse to the mean temperature of the atmospheric column.

In fact, in the equatorial zone, the surface of the earth, including the atmosphere which covers it, may be considered as a cylinder, the tropical circles of which would form the two bases, and the half of which is always illuminated by the sun. This cylinder receives each instant all the heat which falls upon the rectangle of its projection, the surface of which is $2rh$; it receives therefore each minute a quantity of heat

$$1{\cdot}7633 \,.\, 2rh.$$

But this quantity of heat being distributed over the whole lateral surface of the cylinder or upon an extent $2\pi rh$, it is evident that each unity would only receive for its share

$$\frac{1{\cdot}7633}{\pi} = 0{\cdot}56.$$

Such is the quantity of solar heat which on an average falls daily every minute on each square centimetre of the equatorial zone.

At the same time the heat of space also exerts its action, and if we designate by t' the unknown temperature of space, it is easy to see that the quantity of heat received per minute and per square centimetre is

$$\mathrm{B}a^{t'}.$$

Consequently the sum of the quantities of heat received is

$$\mathrm{B}\,a^{t'} + 0{\cdot}56.$$

But the combined effects of space and of the sun may be replaced by a single inclosure, of a maximum emissive power; and if we represent by v the unknown temperature of this inclosure, capable of producing the same effects, or rather capable of transmitting the same quantity of heat, we shall have

$$\mathrm{B}\,a^{v} = \mathrm{B}\,a^{t'} + 0{\cdot}56;$$

it is true that the action of the sun is intermittent, since it ceases to be felt during the night, and during the day it is felt with different intensities at different hours; but these intermittences, producing the variations of temperature which we observe during the day and the night, do not interfere with the exactness of the preceding equation; nor do they prevent the conditions

of equilibrium of diathermanous envelopes applying rigorously to the inclosure, whose unknown temperature we have just designated by v.

This temperature v must therefore be such that it may produce on the surface of the earth, between the tropics, the mean temperature of 27°·5, which results from observation. But we have seen that the excess of temperature of the globe over the inclosure is always deduced from the formula

$$a^{t-t'} = \frac{2-b'}{2-b},$$

t being the temperature of the globe, and t' the temperature of the inclosure.

Now, here, the temperature of the globe being 27°·5, and that of the inclosure v, we must therefore have

$$a^{27°\cdot5-v} = \frac{2-b'}{2-b}.$$

If we take the value of a^v which thence results, and substitute it in the preceding equation, and also for B its value 1·146, we find

$$a^t = 1\cdot235\,\frac{2-b}{2-b'} - 0\cdot489.$$

And as the whole of the solar experiments gives $b' = 0\cdot35$, we arrive definitely at the equation

$$a^{t'} = 1\cdot008 - 0\cdot748\,.\,b, \quad . \quad . \quad . \quad . \quad (5.)$$

in which the only unknown values are the temperature of space t and the absorbing power b, which the atmosphere exercises upon the terrestrial heat.

The greatest value of b gives the lower limit of the temperature of space; and since b cannot be greater than 1, the temperature of space cannot be lower than

$$-175°.$$

For $b' = 0\cdot3$ we should find -187, and for $b_{,} = 0\cdot4$ only -164.

This lower limit once being found, it is easy to ascertain also the superior limit; for it corresponds to the smallest value which it is possible to attribute to b: now the experiments of zenithal temperature showing that b is necessarily greater than 0·8, it results that the temperature of space is less than

$$-115°.$$

To determine now the intermediate number, comprised between these limits, which represents the true temperature of space at the present period, numerous experiments will doubtless be requisite, extending to all latitudes and all heights.

The only experiments that I have yet been able to make permit us to arrive however at a certain approximation; they give

$$-142^{\circ}$$

for the temperature of space, and I do not think that this value can be far from the truth; it corresponds to $b = 0{\cdot}9$. Thus we see, as the definitive result of these researches, that the sun imparts to the earth a quantity of heat 1·7633 per minute and per square centimetre, that with a clear sky the atmosphere absorbs about four-tenths of this heat and of that of space; that it absorbs nine-tenths of the heat emitted by the earth, and that the temperature of space at the present period is 142° below zero. We can scarcely draw attention too strongly to the important part which the inequality of the absorbing powers of the atmospheric air exercises on the whole of the terrestrial phænomena, and consequently to the care necessary to determine them with accuracy. For this purpose doubtless other apparatus and other methods of experimenting will be soon invented, by means of which it will be possible to separate at every instant the complex influences of the radiation of space and the atmospheric radiation. If at the present time the different regions of the sky which pass successively to the zenith appear to us to transmit equal quantities of heat, it is very probable that this only results from the imperfection of our apparatus: we perceive such differences in the nature, distance, number and grouping of the stars in the depths of space, that it is impossible to admit that the portion of the heavens, incessantly changing, which is above the horizon, resembles constantly the portion that is below; and consequently it is impossible that all the hemispheres which we can conceive in the celestial vault transmit really to the earth the same quantity of heat. It is especially in the equatorial zone that we must first seek to appreciate these differences, because they must doubtless appear there greater, more regular and more easy of observation.

23. The following table contains the result of experiments made with the actinometer: the progressive depression of the zenithal temperature will be remarked; the last column of this table contains the mean temperature t'' of the atmospheric column at Paris, corresponding to each observation, and calculated by the formula (4) of the zenithal temperature in which this quantity t'' remains alone unknown.

Table of the Mean Temperatures of the Atmosphere which correspond to the observations of the Actinometer made during the months of April, May and June.

Days.	Hours.	Temper. of the air.	Temper. of the Actinom.	Differ.	Zenithal temp.	Mean temp. of the atmosphere.
		From the 10th to the 11th of April.				
April 10.	7h evening.	10·2	3·9	6·3	— 4·0	—23·5
	8	9·9	3·0	6·9	— 5·6	—25·5
	9	9·6	2·2	7·4	— 7·0	—27·0
	10	9·0	1·8	7·2	— 7·2	—27·5
... 11.	5 morning.	5·0	—3·0	8·0	—13·0	—35
	5 30′	5·0	—3·0	8·0	—13·0	—35
	6	5·5	—2·3	7·8	—12·0	—34
		From the 14th to the 15th of April.				
April 14.	7h evening.	8·5	0 8	7·7	— 6·0	—26
	8	7·0	—0·5	7·5	— 9·9	—30·0
	9	5·8	—1·6	7·4	—10·8	—32
	10	5 0	—2·4	7·4	—11·6	—33·5
... 15.	4 30′ morning.	1·0	—6·0	7·0	—14·7	—37·5
	5	1·0	—6·0	7·0	—14·7	—37·5
	6	1·6	—5·2	6·8	—13·7	—36·0
		From the 20th to the 21st of April.				
April 20.	8h evening.	5·6	—0·8	6·4	— 8·8	—29·5
	9	4·5	—2·0	6·5	—10·1	—31·5
	10	3.6	—3·0	6·6	—11·7	—33·5
... 21.	4 30′ morning.	0 0	—7·0	7·0	—15·7	—38 5
	5	0·0	—7·0	7·0	—15·7	—38·5
	5 30′	0·1	—6·5	6·6	—14·5	—37·0
		From the 5th to the 6th of May.				
May 5.	5h evening.	25·50	19·9	5·6	+12·9	— 2·0
	6	25·10	17·5	7·6	8·0	— 8·0
	7	23·10	15·0	8·1	4·9	—12·0
	8	22·9	13·9	9·0	2·6	—15·0
	9	21·5	12·5	9·0	1·4	—16·5
	10	17 5	10	7·5	0·6	—17·5
... 6.	4 morning.	12·1	5	7·1	—3·9	—23·5
	4 30′	12·1	5	7·1	—3·9	—23·5
	5	12	6	6·0	—1·5	—20·0
		From the 23rd to the 24th of June.				
June 23.	7h evening.	20·0	12·0	8 0	+2·0	—16·0
	8	17·8	10·5	7·3	1·4	—16·5
	9	17·6	10·7	6·9	,,	,,
	10	16·3	9·2	7·1	0·3	—18·0
... 24.	4 morning.	11·3	5·3	6·0	—2·2	—21·0
	4 30′	11·5	5·6	5·9	—1·8	—20·5

24. It seems to me still necessary to indicate some of the most general consequences which result from these researches.

The total quantity of heat which space transmits in the course of a year to the earth and to the atmosphere is deduced from the preceding observations: it is easy to see that this quantity of heat would be capable of melting upon our globe a stratum of ice of

26 metres thickness.

We have seen that the quantity of solar heat is expressed by a stratum of ice of

31 metres.

Thus, together, the earth receives a quantity of heat represented by a stratum of ice of

57 metres,

and the heat of space concurs in this for a quantity which is five-sixths of the solar heat.

Between the tropics, the heat of space is only two-thirds of the solar heat; for the latter is there represented by a stratum of ice of

39 metres.

It will excite astonishment doubtless that space, with its temperature of $-142°$ below 0, can impart to the earth a quantity of heat so considerable that it is nearly equal to the mean heat which we receive from the sun; these results appear, at first sight, so contrary to the opinion which we form, either of the cold of space or of the power of the sun, that we shall be perhaps disposed to regard them as inadmissible. However, we must remark that, with regard to the earth, the sun occupies only five-millionths of the celestial vault, and that it must consequently transmit 200,000 times more heat to produce the same effect.

In considering the phænomena under another point of view, we shall be led, on the contrary, to suppose that in these valuations the power of the sun is much exaggerated; for if we examine the temperatures instead of examining the quantities of heat, we arrive at this result:—

That if the sun's action were not felt upon our globe, the temperature of the surface of the ground would throughout be uniform and at

$-89°$.

Now, since the mean temperature of the equator is $27°{\cdot}5$, we

must conclude that the presence of the sun augments the temperature of the equatorial zone by

$$116°{\cdot}5.$$

In the same manner, the mean temperature of the atmospheric column would be at the equator

$$-149°.$$

The preceding formulæ show that it is about $-10°$; thus, the intermittent presence of the sun increases by

$$139°$$

the mean temperature of the entire atmosphere in the torrid zone. This effect of the sun to augment the terrestrial temperatures much exceeds that which M. Poisson obtained in considering the variations of temperature at different depths beneath the surface of the ground; but it appears to me that the two methods will yield results more accordant, when we can introduce in a more direct manner, into the formulæ, the influence of the atmosphere, which is so considerable.

To extend these calculations to other regions, we must take into account the decrease of the temperature of the ground in proportion as the latitude increases; but, by approximation, it is easy to recognise that the effects of the wind concur to raise the temperature of the polar regions, by lowering more or less the temperatures of the regions comprised between the polar and tropical circles; the temperature of the equatorial zone itself appears little lowered by this cause.

The object of this extract is especially to give an idea of the theoretical principles and the experimental methods which serve as the basis of this investigation. I may be allowed to invite the attention of geometricians and natural philosophers particularly to these two points: with respect to the numbers which result from my experiments, they will have to be modified; subsequent researches, simultaneously undertaken on different points of the globe, will be necessary to give them all the precision which they require.

NOTE 1.

The mode of demonstration which I have used in this article permits the solution of several difficulties which are still presented by the most fundamental principles of radiant heat,—namely, the principle of the equality of temperature and of the equality of the emissive powers of two surfaces which do not reflect; the law of the cosinus; and the law of emission, considered in relation to the constant which the calculation gives, and which is added to the function of temperature.

Principle of the equality of temperature and of the equality of the emissive powers of two surfaces which have no reflective power.—It may be admitted as evident, that two equal surfaces of the same matter, both possessing a maximum emissive power, emit equal quantities of heat in the same time, when they have equal temperatures; for, all being identical, the quantities of heat emitted must be themselves identical.

Thus, for this particular case, if the globe and the inclosure have the same temperature, we have $e = e'$, the equilibrum is established, and we have at the same time $b = \sin^2 \omega$.

This result is independent of the dimensions of the globe and the inclosure: now, the same globe, at the same temperature, losing always the same quantity of heat in the same time, it results that all the inclosures, large or small, transmit to the globe the same quantity of heat; it results, consequently, that at any portion of a given inclosure, seen from the centre of the globe at a certain angle, we may always substitute a portion of another inclosure seen at the same angle; this tends to prove that the temperature of the globe is equal to that of the inclosure, not only when it is at the centre of that inclosure, but whatever be the position that it occupies.

If now the globe is not of the same substance as the inclosure, if, in a word, it ceases to be identical with it, without ceasing to have, like it, a complete absorbing power, the loss of the globe will then be $e_1 s$; the portion of heat which it receives from the inclosure and which it absorbs will always be the same, namely, $e' s' \sin^2 \omega$; and the sole condition required for the equilibrium will in like manner be, that the quantities of heat lost and absorbed may be equal, which gives again

$$e_1 s = e' s' \sin^2 \omega,$$

whence

$$e_1 = e';$$

that is to say, even in this case it is necessary for the equilibrium that the unity of the surface of the globe loses in the same time as much heat as the unity of the surface of the inclosure.

It remains to examine whether, to undergo this loss, the globe must still have the temperature of the inclosure: now, if it must have, for example, a higher temperature, this excess being independent of its dimensions, it would be necessary that it should preserve it when it had sufficient volume to fill the inclosure; whence it follows that there might be a permanent difference of temperature between two bodies which touch, or at least which are very near to one another, a thing that is contrary to all experiments.

Thus, two equal surfaces, possessing a complete absorbing power, always emit equal quantities of heat when they are at the same temperature, whatever be the difference of matter or property between them.

It is evident that, in this case, the principle of the equality of temperature, at equilibrium, cannot be demonstrated *à priori*, and that it results only from the general indications of experiment.

But the second principle, that of the equality of the emissive powers of any two surfaces of the same temperature, which do not reflect, is immediately deduced from the first; it is upon this point that some uncertainty remained*.

Law of the Cosinus.—The law of the cosinus, which appears to leave a doubt on the mind of some natural philosophers†, is also deduced in a very simple manner from the same considerations.

Since for the equilibrium we have always $e = e'$ and $b = \sin^2 \omega$ where the globe and the inclosure have complete absorbing powers, and since each unity of surface of the inclosure transmits to the globe a quantity of heat expressed by $e \sin^2 \omega$, ω being the angle of emission, that is to say, the angle of the extreme rays with the normal on the surface, it is evident that, for an angle ω' a little larger than ω, the quantity of heat would be

$$e \sin^2 \omega';$$

whence it follows that the quantity of heat emitted in the zone comprised between ω' and ω is

$$e (\sin^2 \omega' - \sin^2 \omega);$$

the surface of this zone being $2\pi (\cos^2 \omega - \cos \omega')$, the quantity of heat emitted from the corresponding unity of surface is therefore

$$\frac{e}{2\pi} (\cos \omega + \cos \omega'),$$

or

$$\frac{e}{\pi} \cos \omega,$$

supposing that the difference is very small between ω and ω'.

That is to say, if we consider the element of a radiating sur-

* M. Poisson, *Théorie de la Chaleur*, p. 42. † Ibid. p. 35.

face as the centre of a hemisphere whose radius is equal to unity, and if we call e the total quantity of heat emitted by this element in all directions, the quantity of heat emitted on a single element of the hemisphere, which is at an angular distance ω from the normal, is expressed by

$$\frac{e}{\pi}\cos\omega,$$

and is consequently proportional to the cosinus of the angle of emission, this angle being reckoned to begin from the normal.

It is easy, starting from this value, to re-ascend by integration to the primitive expression $e \sin^2 \omega$.

This demonstration is perhaps more elementary than that which has been given by M. Fourier*; it does not suppose any consideration relative to the temperature, and applies consequently to all temperatures; it is deduced from a single condition, which is, that we have $b = \sin^2 \omega$, and, as the quantity of heat which the globe receives from the inclosure is independent of the heating or the cooling of the globe itself, we see that it is not less strict for the case of heating or cooling than for the case of equilibrium.

Constant of Emission.—After having found the relation

$$m\,a^{\theta} + \text{constant},$$

MM. Dulong and Petit remark (page 74) that it represents the total radiation of the inclosure, and that, the origin of the temperatures being arbitrary, we may assume it so that the constant may be null, which would reduce the expression to $m\,a^{\theta}$.

But there remains some difficulty upon this point; for, in choosing the 0 of the thermometric scale so that θ may be equal to $-\infty$, the first term is null, and the constant remains, so that it could only disappear by admitting that it must have a negative value: moreover, the value of m necessarily changes with the origin of the temperatures; it diminishes in proportion as the origin descends and as the temperatures are represented by greater numbers, and reciprocally; in short, the value of m is such, that the total radiation of the inclosure appears expressed rather by a temperature than by a quantity of heat, and nevertheless it is difficult to conceive how the total radiation of the inclosure can be expressed by a temperature or by a number of degrees lost or gained.

On another side, M. Poisson†, on comparing the functions to which he has arrived and those of the law of cooling of MM. Dulong and Petit, preserves the constants in the first functions, and suppresses them in those of the law of cooling, which re-

* *Annales de Chimie et de Physique*, tom. iv. p. 135.

† *Théorie de la Chaleur*, p. 42.

verts to the supposition that they are different in the two cases; but it must be remarked that all the experiments which can be made being relative to changes of heat in which these constants are destroyed, no observation can ever give their value.

There remains therefore respecting this constant of emission a theoretical difficulty the more serious, because upon it alone depends the impossibility of considering the absolute emission and of assigning a value to the real and total quantities of heat which are emitted by the radiating surfaces. It appears to me, however, that this difficulty is not incapable of solution: the constant in question is only a product of the calculation; it cannot represent any mechanical condition nor any physical phænomenon, and its value must be null in all cases.

Let us in fact suppose that e, or the total quantity of heat emitted by the unity of surface of a body during the unity of time, be represented by the known function of the temperature, *plus* a constant, so that we have

$$e = \mathrm{B}.f.a^{t+\theta} + \mathrm{C},$$

and let us determine the laws of cooling, by supposing that the inclosure has a complete absorbing power, whilst the globe has only an absorbing power represented by b'.

Let θ be the temperature of the inclosure, e' the quantity of heat which it emits from the unity of surface in the unity of time, and 1 its emissive power: the total quantity of heat lost by the globe will be

$$e\,s;$$

the quantity of heat emitted from the unity of surface of the inclosure being e', the portion which reaches the globe is always

$$e' \sin^2 \omega;$$

the globe only absorbs a portion b', consequently a quantity

$$b'\,e' \sin^2 \omega,$$

and it absorbs together of that which it receives from the entire inclosure,

$$s\,b'\,e' \sin^2 \omega = s\,b'\,e';$$

its definitive loss is therefore

$$e\,s - s\,b'\,e'.$$

But if we have

$$e = \mathrm{B}f.a^{t+\theta} + \mathrm{C}, \qquad e' = \mathrm{B}.a^{\theta} + \mathrm{C},$$

this loss of heat becomes

$$s\,\mathrm{B}f(a^{t+\theta} - a^{\theta}) + s\,\mathrm{C}(1-f),$$

because the radiating power f of the globe is equal to its absorbing power b'.

Let p be the weight of this globe, c its capacity for heat; for a loss of heat $p\,c$, it loses in temperature 1°; and, for the loss expressed above, it loses in temperature a number of degrees expressed by

$$\frac{s\,\mathrm{B}f}{p\,c}(a^{t+\theta}-a^{\theta})+\frac{s\,\mathrm{C}}{p\,c}(1-f).$$

Such is the rapidity of cooling.

For this result to coincide with that of MM. Dulong and Petit, we must have

$$m=\frac{s\,\mathrm{B}f}{p\,c}\text{ and }\mathrm{C}=0.$$

Now MM. Dulong and Petit having submitted to experiment a silvered thermometer in a blackened inclosure, and the perfect accuracy of the law of cooling having been thus verified in the most exact manner, we see that the constant of emission is necessarily equal to zero in this particular case, and consequently it is always null in all possible cases.

We must therefore, without exception, employ the formula

$$e=\mathrm{B}.f\,a^{t},$$

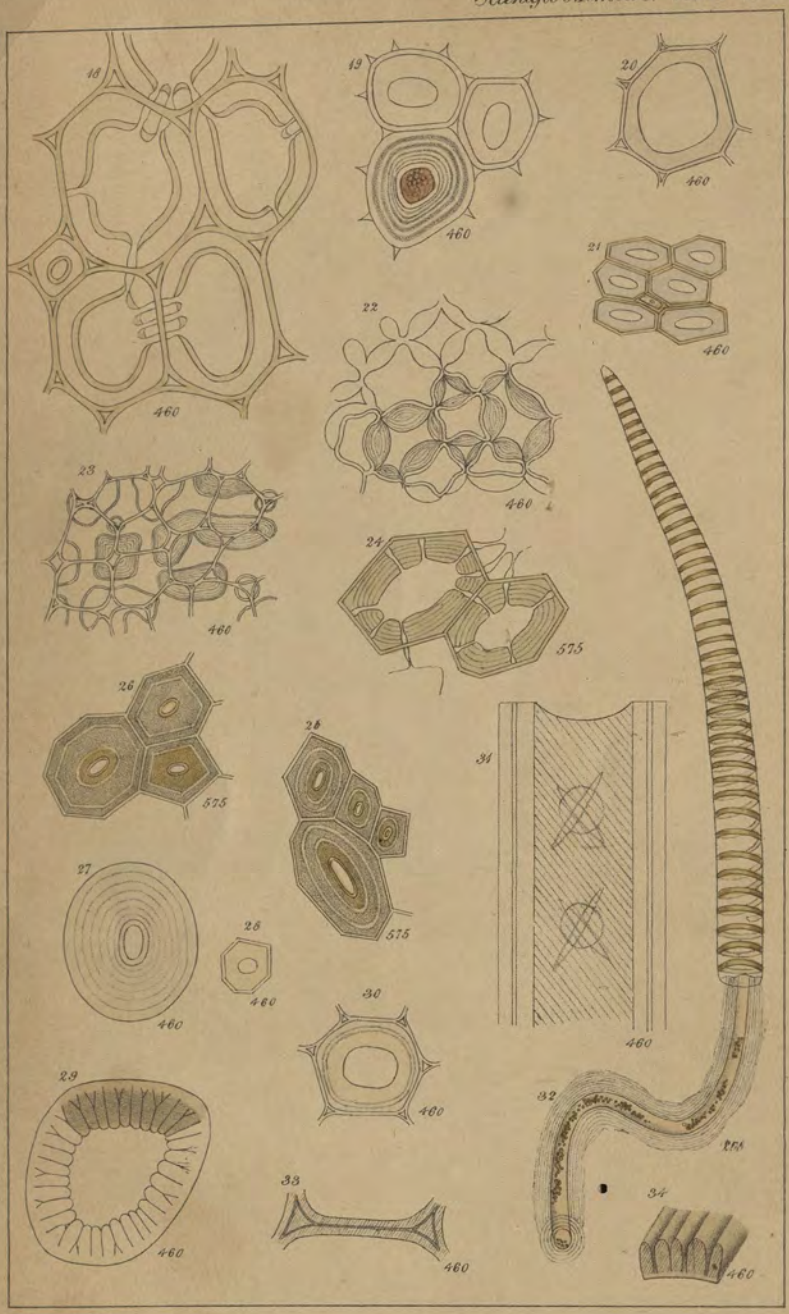
at least throughout the extent of the scale for which the law of cooling is demonstrated. The constant B is, as I have said, an invariable constant, the numerical value of which depends on the unities of surface and of time which we select and on the point whence we reckon the temperatures, whilst the numerical value of a depends on the number of degrees or divisions which we establish between the two fixed points which serve as a base to the thermometric scale. If, for example, we raised the zero of the scale 100°, preserving for the degree the magnitude which it has actually in the centigrade scale, a would remain equal to 1·0077, and the value of B would have to be multiplied by a^{100}.

With respect to the radiating power f, we may remark that, for athermanous substances, its value only depends absolutely upon the state of the surface, and appears to be comprised between $\frac{1}{10}$ and 1 for all known surfaces: but, in diathermanous substances, f depends both upon the state of the surface and upon various other properties of these substances. It will now be an essential point for the theory of heat to determine what are the properties which may modify the value of f, and the part of the influence which pertains to each of them in these variations.

Note II.

I have made a great number of experiments with the actinometer, exposing it perpendicularly to the solar rays at different

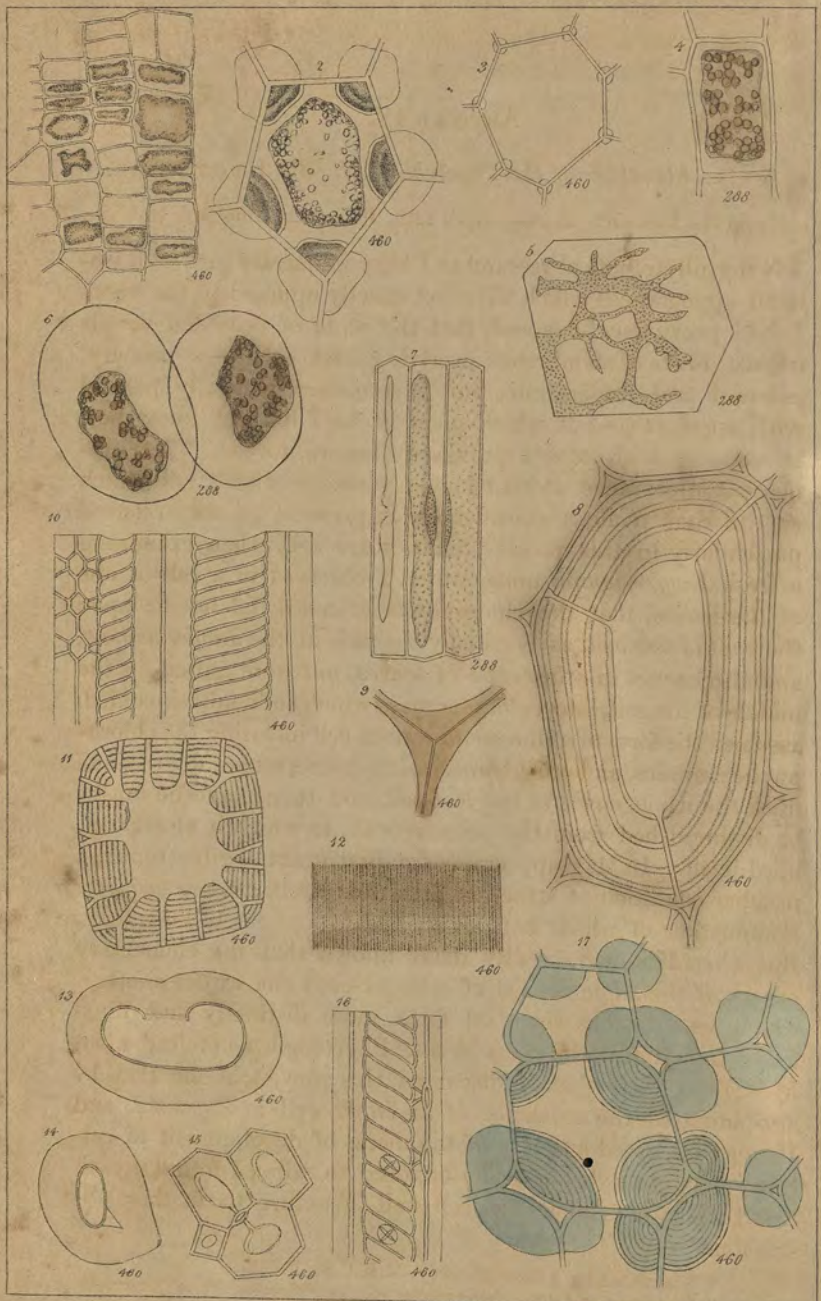
hours of the day: its central thermometer then assumes considerable elevations of temperature; it often rises to 50° above the ambient temperature towards noon, and it sometimes even rose to 90°, the temperature of the air being 27°, which gives an elevation of 63°. I point out these results only to show, on the one hand, that the actinometer might be graduated by the pyrheliometer, if we only desired to have approximate results of the solar heat; and to show, on the other hand, that thermometers exposed to the sun may, according to the dispositions given them, take any required excess above the temperature of the air from 3° or 4° up to 63° or 64°.



Mohl *on the structure of the Cell.*

R. E. D. lith.

prel. lith. Linn. imp. 6 King William Street, Strand.



Mohl *on the structure of the Cell.*

R. E. B. lith.

prel: lith: Linn: imp: 8, King: William Street, Strand.

Article IV.

On the Structure of the Vegetable Cell. *By* Hugo Mohl.

[From the *Botanische Zeitung*, April 12th, 19th, 26th; May 3rd, 10th*.]

IN my phytotomical researches I have frequently met with isolated appearances which were not exactly opposed to the views I had previously advanced, that the septa of cells and vessels consist of two membranes overlying each other,—a primary, external and imperforate, and a secondary generally pierced with apertures,—but which phænomena I did not know how to connect with others previously known to me. An evanescent appearance which I had only once met with, and which at the time made a considerable impression on me, referred particularly to this point. Some years ago, when examining a fresh *Jungermannia* under water, I observed in a cell of one of the leaves, that the chlorophylle granules did not lie upon the wall of the cell, as is usually the case in the *Jungermanniæ*, and also occurs in other cells of leaves, but were united, in the middle of the cell, into a globular mass which suddenly expanded, assumed the form of a thin membranous cell inclosing the chlorophylle granules, and quickly increasing in size, after a few seconds filled the whole space of the leaf-cell, and then could no longer be distinguished from the primary wall, to which it closely applied itself. In this appearance, at first unintelligible to me, a peculiar condition of structure presented itself, a more accurate examination of which baffled my endeavours for a long time. But when Kutzing recently made known that the elementary organs of the Algæ consist of cells inclosed one within another, which view he has since set forth more distinctly and illustrated by beautiful drawings in his 'Phycologia generalis;' when Meneghini, with whom I discussed this view, told me that he also admitted the existence of an inner cell in *Zygnema*, and Hartig† advanced a theory of the mode of development of cellular membrane diametrically opposed to mine, I found myself called upon to submit the cell-wall structure to further observation.

* Translated by Arthur Henfrey, M.R.C.S., F.L.S.

† *Beiträge zur Entwicklungsgeschichte der Pflanzen.* 1843.

Since the results of this investigation are treated of in the following pages in more particular relation to Hartig's memoir, a short abstract of the principal points of his theory will not be considered superfluous. According to him, the cell-wall structure consists of three superposed layers. The innermost, the *ptychode*, is the first developed; the ptychodes of young cells are consequently in immediate contact with each other, and cohere either at isolated, round spots, or in bands running in a spiral direction. At a later period, there separates, at the points where no cohesion has taken place, a mass which by solidifying becomes that layer which I have called secondary cellular membrane, and to which Hartig has given the name of *Asthate*; lastly a common cement of both cells, the *Eusthate*, forms between the asthates of two neighbouring cells. This is the layer which has hitherto been regarded as the primary membrane; in many cases it does not extend over the whole periphery of the cell, but is limited to points in the vicinity of an intercellular passage. These three layers differ in their behaviour towards iodine and sulphuric acid. If, for instance, a cell be moistened with tincture of iodine, and then some dilute sulphuric acid allowed to act on it, the ptychode and the eusthate will be coloured yellow, while the asthate will become blue and swell considerably. This difference of colour not only allows the ptychode to be distinguished from the asthate, but shows also that the former clothes the dotted ducts.

1. *The Primordial Utricle.*

My observations were first directed to the detection of the ptychode. The following is the result:—

If we examine a yearling shoot of a tree or the stem of an annual plant which, before the completion of its longitudinal growth, has been placed in spirit and kept there some time, we find in all the cells and vessels whose secondary layers have not attained their complete development, an inner membrane which is remarkably distinct from the other membranes of the cell. This membrane forms a completely closed, thin-walled, cell-like vesicle, which, in the fresh plant, is closely applied to the inner wall of the cell, and therefore escapes observation, but by keeping the specimen for some time in spirit becomes contracted and more or less detached from the cell-wall. In specimens

which have remained for a number of years in spirit, this membrane exhibits a yellowish colour, and is then easily detected; in those which have only been some months in spirit it is uncoloured, very transparent, and easily overlooked. In such cases it is readily rendered visible by weak tincture of iodine, which imparts to it a yellow or brown colour. I found this inner cell-like structure, which for reasons to be mentioned hereafter, I shall call the primordial utricle (*Primordialschlauch*), *utriculus primordialis*, in an equally perfect condition in a series of dicotyledonous plants which I examined in the manner above mentioned, viz. in *Sambucus Ebulus* (fig. 7. Plate I.), *Ficus Carica*, *Pinus sylvestris* (fig. 1), *Asclepias syriaca*, *Hoya carnosa*, *Euphorbia canariensis* (fig. 6), *Caput medusæ*, &c. In the Monocotyledons it may be detected in a similar manner in the cells at the apex of the stem and root. Since it occurs in every plant in which I have looked for it, its universal existence cannot be doubted.

The primordial utricle is present in all or only in a portion of the cells and vessels, according to the age which the shoot has attained. In very young internodes, only a few lines long, in which the woody column has begun to form, and as yet consists in all its parts of thin-walled elementary organs, the primordial utricles occur in all the cells and vessels; this is not the case at a later period, when the woody column is more perfect. Half-developed internodes, therefore, will be the best adapted for obtaining a view of the relation of the primordial utricle to the development of the cell-wall structure. In such half-developed internodes we find the primordial utricle, under the form of a perfectly closed cell, in all the elementary organs of the bark, the cambium layer and the medulla, but no longer in the cells and vessels of the wood whose walls have already become thickened. In all cells which contain granular formations (chlorophylle granules, starch granules, &c.), these lie within the primordial utricle, and have separated with it from the cell-wall; when the nucleus of the cell is still present, as in the cells of the cambium layer (fig. 7. Plate I. from *Sambucus Ebulus*), this also lies within the primordial utricle and is usually adherent to its inner wall; more rarely it is in the centre of the utricle, in which case it is maintained in connexion with the walls by mucilaginous threads. The wall of the primordial utricle is not altogether smooth like the cell-wall, but finely granular. In the

specimens kept in spirit, it offers sufficient resistance to the knife to allow of its being cut through by a transverse section, like the cell-wall, and will then be found in the form of a more or less wavy ring in the cavity of the cell (fig. 1. from *Pinus sylvestris*). Not unfrequently the primordial utricle lies quite loose in the cell, and hence often falls out of a delicate transverse section. If dilute sulphuric acid is applied to a preparation which has been treated with iodine, the previously uncoloured cell-walls swell up and are stained blue, while the primordial utricle does not alter in form, but acquires a darker yellowish-brown colour. In concentrated sulphuric acid this membrane loses its continuity.

The foregoing observations might lead to the conclusion that Hartig was acquainted with the primordial utricle and had described it under the name of ptychode, but it will presently be shown that by this name Hartig meant something totally different. He describes the ptychode as the most internal membrane of full-grown cells and vessels, while in these all traces of the primary utricle have long since disappeared. For if we follow this out in internodes of medium growth, it is evident that it undergoes the most essential modifications, with the increased age of the cells. These changes commence simultaneously or at shortly succeeding periods, in various portions of the stem, in the innermost layer of the wood, in the cells of the middle layers of the bark, and in the centre of the medulla, extending with the increasing age of the plant from these points to the rest of its structure. These changes are more easily traced in parenchymatous than in prosenchymatous cells or dotted ducts, both on account of the greater size of the cells and of the slighter thickness and greater transparency of their walls. In general they consist in this: as the cell grows older and its wall becomes thickened by the deposition of secondary layers, the primordial utricle becomes proportionately thinner and proceeds towards its dissolution. Two modifications of the way in which this takes place present themselves. We either find, as in the older cells, the primordial utricle adhering more firmly to the cell-walls, and applied over the inner surface of the cell in the form of a thin coating, in which case it may be detected by the yellow colour it assumes with iodine and by its finely granular structure; or, as in the younger cells, it is detached from the cell-membrane, no longer however in the form of a closed cell, but as an irregular web

with broader and narrower membranous appendages and threads covered with fine granules, similar to those mucous reticulations (which are coloured yellow by iodine), frequently met with distributed over inner walls of fresh cells. The first modification occurs in the medullary cells of *Pinus sylvestris*, the second in those of *Asclepias syriaca* (fig. 5). If we examine still older internodes the primordial utricle will have finally disappeared without leaving a trace of its existence; this happens at different periods in different plants, earlier in woody than in succulent; in which latter the primordial utricle will be found in perfection at a later period in the medullary, and particularly in the bark cells of *Cactus* and the fleshy *Euphorbiæ* (fig. 6).

That the primordial utricle disappears in an analogous manner in the elementary organs of the wood, soon after the deposition of the secondary layer commences, is easily seen both in the vessels and ligneous cells of Dicotyledons and in the punctated tubes of the Coniferæ.

As we trace the primordial utricle to its origin, the difficulty of observation and the uncertainty of its result increase in proportion as the cell is younger, because the question of its origin is complicated with that very difficult question, the origin of the cell. In the examination of the apex of the stems or the root of all plants, in the act of development, and of the cambium layer of Dicotyledons, we find a cellular tissue, which (setting aside the slight thickness of its walls) differs from the tissue of the more developed parts, by a very close application of its cells to each other so as to exclude entirely intercellular passages, and also by the unequal thickness of the cell-walls. On this last circumstance Unger has already very properly laid great stress; it is especially striking in the cambium layer, in which the cell-walls lying parallel with the bark are thinner than those parallel with the medullary ray, as is shown in fig. 1, which exhibits a transverse section of the cambium layer of *Pinus sylvestris*, where however the distinction between the different cell-walls is much slighter than in many Dicotyledons. Bearing some though not very striking analogy to this, the young organs in parenchymatous cells also not unfrequently present thinner transverse walls, especially in the green bark, in the cells of which the thin transverse walls generally have a direction perpendicular to the surface of the bark.

Since we see then, in these instances, and especially in the

cambium layer, places where the number of elementary organs continually augments without any interruption of the continuity of the tissue, or any spot where a new elementary organ could insinuate itself between those already formed, being discoverable, two modifications only of the process of cell-generation are probable,—the division of the older cells by the formation of a septum, or the formation of cells within cells. In each of these young cells, without exception, a primordial utricle may be found; the origin of this, therefore, is at least contemporary with the formation of the cell itself. If it could be positively ascertained, that in cells which are in the act of increase two primordial utricles exist near together before the septum is developed between them, it would be decided, as far as relates to the cambium layer and the apex of stems and roots, that here the formation of the primordial utricle precedes the formation of the cell, and the name I have applied to it would be justified. I believe that I have actually observed this process repeatedly, especially in the cambium layer of *Pinus sylvestris*, *Sambucus Ebulus*, *Asclepias syriaca*, in the bark cells of *Rhus typhinum*, in a young leaf of a *Sempervivum*, and in the apex of the stem of *Euphorbia Caput medusæ*; since, however, the transverse septa, at their first appearance are particularly delicate, and it being very possible that the deficiency of the transverse wall between two primary cells was only apparent and consequent on a rupture of it, I dare not venture to publish these observations as absolute facts, although I took every care to remove any sources of illusion. Since each young cell contains a primordial utricle, either this must be absorbed before the increase of the cell commences, to make room for two new ones originating in its place, or the old primordial utricle must separate by constriction into two; I could not succeed in ascertaining the most minute details by observation, but the former is the more probable, as the formation of the primordial utricle in vascular plants is always connected with the formation of the nucleus*. Unger† first announced that the

* The division of the cells which takes place in Confervæ is probably a totally different process from the multiplication of cells in vascular plants; at least I find no nucleus in the true Confervæ, and have never seen, in Phanerogamous plants, a constriction of the primordial utricle by a septum growing from without inwards, similar to that which occurs in the Confervæ, in which the primordial utricle continues, without interruption and without a transverse septum, through the constricted part until on perfect strangulation it separates into two distinct utricles.

† *Ueber die Genesis der Spiralgefässe*, *Linnæa* xv. 385.

formation of the nucleus of the cell is always subsequent to the origin of the cells; I cannot, however, agree with this statement. It is quite true that frequently, and especially in the roots of Monocotyledons (on the observation of which Unger founded this view), the nuclei do not attain their full size and shape for a long time after the formation of the cell, but they may be proved to exist along with the nucleolar granules even in the youngest cells, by the use of iodine, and considering the analogy of those cases in which the formation of the cell is more clearly to be traced, as in hairs, must be regarded as the organ preceding the cell. On the whole I am inclined to consider the foregoing observations as confirmatory of Schleiden's theory respecting the formation of cells*; on two points, however, I cannot but differ from Schleiden's views. One refers to the connexion existing between the nucleus and the nascent cellular membrane. Schleiden's says that the latter grows out from the nucleus in such a manner that it is applied upon it like a watch-glass, and the nucleus forms part of the developed cell itself; to me, on the contrary, the cell membrane always appears to surround the nucleus, in the form of a closed vesicle, and in many cases to lie at some distance from it, even at their first origination, so that in this case the nucleus is by no means in immediate contact with the cell-membrane. The second point relates to the nature of this primary cellular membrane. According to Schleiden's view this is the membrane which forms the future external membrane of the cell; to me it appears to be that which has hitherto been described as the primordial utricle. If, for instance, we examine young cellular tissue, the nucleus will be found in particularly close connexion with the primordial utricle. Either, and this is usually the case, (occurring, for instance, without exception, in the cambium layer,) the nucleus lies immediately on the primordial utricle, and separates with it from the permanent cell-wall, or threads proceed from the mucilaginous coating of the nucleus, which connect it with the primordial utricle, so that frequently it is suspended, as in a cobweb, in the middle of the cell; this is most beautifully seen in *Zygnema*, in which Schleiden mistook these threads for currents of sap; in other cases the whole space between the nucleus and the primordial utricle is filled with vesicular formations, whose walls consist of the same mucilaginous

* See Scientific Memoirs, vol. ii. p. 281.

granular substance as the threads and the immediate envelope of the nucleus, and which like the primordial utricle itself are coloured yellow by iodine. Even this intimate connexion of the nucleus with the primordial utricle must render it more probable that the latter is the first cellular membrane than that the outer cell-membrane is formed first, and that the primordial utricle subsequently insinuates itself between it and the nucleus, separates the latter with its mucilaginous appendages from the external cellular membrane, and forms around it a new cell-like envelope. The point however would be incontestably proved by the above-mentioned observations, that two primordial utricles lie contiguous in the still undivided cavity of the cell, if indeed no illusion was mixed up with those observations.

Although the preservation of a plant for a long time in spirit appears to be the best way of detaching the primordial utricle from the cell-wall and rendering it visible, this result may often be obtained by a far shorter process. In general it suffices to submit the preparation for a few minutes to the action of nitric or hydrochloric acid; the acid is then to be neutralized by ammonia, and if the preparation be now coloured by means of iodine, the primordial utricle generally presents itself, as beautifully as in plants which have been kept a long time in spirit, in the form of a vesicle detached from the cellular membrane. It may be detected in this way in the cells of leaves in most cases, for instance, in *Vallisneria spiralis* (fig. 4), *Sanseviera zeylanica*, &c.; it may also be very clearly demonstrated in the leaves of Mosses and Hepaticæ, viz. in *Jungermannia Taylori* (fig. 2), in which latter the primordial utricle may sometimes be distinctly separated from the cell-walls by repeated drying and re-moistening*. The primordial utricle appears to exist, in all those cells of the leaves which contain chlorophylle granules, under the form of a completely closed vesicle; this is not so much the case in the transparent cells which in some plants, *ex. gr. Tradescantia discolor*, lie between the epidermis and the green layer, and in the cells, not coloured green, which form the middle substance of thick fleshy leaves. In the family of the Algæ, the cells of which contain granular formations during their whole life, the primordial utricle does not exhibit the same extent of decay as

* During the progress of the above observation on *Jungermannia*, I had evidently before me a cell in which the primordial utricle had accidentally separated from the cell and had swelled out in the water.

it does in the cells of the stems of the Phanerogamia; it is generally very easily found in these plants, and especially in all those cases where the cells attain a considerable size. In the Fucoideæ, as in *Halidrys siliquosa*, *Furcellaria fastigiata* (fig. 19. Plate II.), it is distinguished from the colourless cell-membrane by its brownish tint, and also by its resistance to the action of sulphuric acid; it is still easier to be detected in the Confervæ, and particularly in the *Zygnemata*, in which latter the action of alcohol and tincture of iodine readily effect its separation from the cell-membrane. It is more difficult to recognise it in Algæ possessing minute cells, as in the *Ulvæ*, in *Bangia atropurpurea*, &c., as there is far more trouble in distinguishing it from the contents of the cell. The same difficulty occurs in the Lichens; the primordial utricle is however to be detected in these, in the green round-celled layer, especially in those species with a dense leaf-like thallus, as *Sticta glomerulifera*. The discovery of the primordial utricle in this family belongs to Wöhler and Knop*, who first found it in *Usnea*.

We may conclude from the foregoing statements that the primordial utricle is very generally distributed, but takes no permanent share in the formation of the cell-wall in the Phanerogamia; but, like the nucleus, is a temporary formation connected with the origin of the cell. The question now arises, whether the primordial utricle is to be regarded as a cellular membrane, or whether it is not rather to be reckoned among the contents of the cell and looked upon as a coagulated mucilaginous coating on the cellular membrane, for which indeed it has certainly been frequently taken, since it has undoubtedly presented itself in some cases, as in *Zygnema*, to every vegetable physiologist, without having been regarded by them as a distinct membrane. The substance of which the primordial utricle is constituted appears to be, if not identical, at least nearly allied to the mucogranular substance which usually invests the nucleus as an irregular mass, and from which run out those mucilaginous threads we meet with so often in young cells, since these parts behave in the same manner towards iodine and sulphuric acid. So far, it is true, we are unable to draw such a distinct line between the primordial utricle and its contents as we can between the permanent cell and its contents; on the contrary, it would appear that the primordial utricle must be considered only as a

* Gœtting. gel. Anz. 1844, p. 22.

part of those still little known, constantly-changing formations (*Gebilde*) which are found accompanying the nucleus in young cells. In spite of this I believe that its substantiality as a distinct organ is beyond doubt, since it is not only present in all young cells as a distinctly marked, perfect membrane, but in many lower plants, as in the Confervæ, it occurs isolated, without nucleus, and is present as a perfectly closed cell in certain organs of the Phanerogamia, especially in the leaf-cells containing chlorophylle and in the fleshy bark, at a period long after the nucleus has been absorbed.

It must certainly be admitted as extremely probable that the primordial utricle is not only intimately connected with the formation of the cell-wall structure, but also with the chemico-organic processes going on in the cavity of the cell, since it forms that organ with which the fluid contents of the cell are in immediate contact. In this respect the fact that the substance of the primordial utricle is entirely distinct from the substance of the permanent cell-wall, as shown by its dark colour with iodine and its insolubility in acid, is clearly of the highest consequence. If the former circumstance might be regarded, as some French chemists maintain, as an evidence of the presence of nitrogen in an organized body, the primordial utricle would either consist of, or be thoroughly imbued with, a nitrogenous substance, and during its existence, the cell-wall structure would be entirely free from nitrogenous combinations, since this is seldom, and then but feebly, coloured yellow by iodine during that period. If this really be the case, it explains a fact long known, but respecting the cause of which no clear idea has ever been entertained. It is well known that young organs abound in nitrogenous compounds and the growth of plants, consequently the formation of new elementary organs consisting of substance free from nitrogen, depends upon the absorption of nitrogenized nutriment. Is not this dependence a proof that the formation of a cell is dependent on the development of a primordial utricle, and that nitrogenous nutriment is absolutely necessary to the formation of the latter?

The transient persistence of the primordial utricle shows however, that although both the origin and the growth of the cell are dependent upon it, the physiological functions of the cell are not all connected with the primordial utricle. In relation to this however it must not be overlooked that we see the prim-

ordial utricle maintaining its perfect integrity in the Phanerogamia, in the cells of the leaves containing chlorophylle granules, and in the outer green cells of the bark, replacing in a physiological point of view the leaves of the fleshy *Euphorbiæ*; that moreover we observe the same in the Algæ, the individual cells of which exist in a great degree independent of one another. Ought we not then to conclude that the primordial utricle takes a part in the assimilation of the crude nutritive juices, as well as in the origination of the cell? But enough of conjectures as to the functions of an organ whose very existence has yet to be admitted by other observers!

Postscript.—I had already written the above when I read M. Karsten's treatise *De Cella Vitali*, from an earlier study of which I had been hindered by accidental circumstances. I perceived from it that its author was also acquainted with the structure which I have called the primordial utricle, that he too accomplished its separation from the cell-wall by the employment of spirit of wine, but that he had advanced a theory of its function directly opposed to that above given, since he ascribes to it an origin subsequent to that of the proper cellular membrane, and holds it to be a secondary cell, formed in the cellular cavity. There consequently existed a contradiction to my observations, even before they were published: this will not matter, but will rather be an inducement for some one else to devote himself to the investigation of this subject. Should my view prove to be untenable, it may be placed in the great chapter of phytotomical errors, if only the truth comes forth in the contest. I will only observe in reference to the representation which Karsten has given of the primordial utricle, that he was indeed acquainted with it, but that nevertheless he confounded it with the secondary layers of the cellular membrane. These two membranes differ from each other as much as any two things can do which have not the slightest connexion with one another.

2. *The Cell-membrane.*

If we now pass from the temporary structure of the primordial utricle to the permanent formation of the cellular membrane, we find the latter always to be composed of at least two layers, an outer, which I regard as the oldest cellular membrane, and an inner, which I consider a secondary deposit. Hartig takes not only a different view in reference to the order of their ori-

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gin, but also affirms the constant existence of a third inner membrane (the ptychode) in all full-grown cells and vessels, which clothes the cells and is imbedded in all the canals of pores.

This latter point first merits consideration. Hartig founds his views of the presence of the ptychode more particularly on the structure of the elementary organs of the wood of *Taxus*, which I believe I demonstrated years ago to be composed of at least three layers. I cannot allow this conclusion from the structure of one formation, not indeed altogether without parallel, but up to this time always regarded as an exception, to be extended to the structure of all other elementary organs.

In reference to Hartig's assertion, that all full-grown cells and vessels possess an inner membrane, the substance of which is essentially distinguished from that of other secondary membranes by its behaviour towards iodine and sulphuric acid, I have examined anew the cells of a tolerable quantity of plants and obtained a negative result. It is generally admitted that the secondary cellular membrane consists of many superposed layers; in a great number of plants any one may convince himself of this in every transverse section of the cellular membrane, I will merely adduce as very striking instances the ligneous cells of *Clematis Vitalba* and the cells of the vascular bundle of the cane (*Calamus* — ?) (figs. 24—26. Plate II.). In many cases, on the contrary, the cellular membrane appears perfectly homogeneous under the best microscopes, even when it has attained some thickness; this is especially the case in the uncoloured, horn-like cells of many seeds, for instance, the albumen of *Phytelephas*, many Palms, *Liliaceæ*, *Rubiaceæ*, &c., and also very frequently in the gelatinous, soft cells which lie under the epidermis of the stem in many plants, as in *Sambucus*, *Spinacia*, and many *Labiatæ*. The application of acids, however, proves that in these cases the cellular membrane is not in reality homogeneous, but equally composed of numerous superposed layers. The softer and more gelatinous the membrane, the sooner does the lamellar structure show itself on the application of nitric or hydrochloric acid, for instance in *Spinacia*; the firmer and more horny its substance, as in many Palms, the more necessary becomes the application of sulphuric acid. No universal directions can be given in reference to the degree of concentration of the acid to be employed, as this must be found by experience in each individual case; but a too weak and a too powerful acid are equally

to be avoided, as the first does not act and the second exerts too strong a disintegrating power on the membrane, under neither of which circumstances can the layers be made out. It is likewise necessary to employ an acid when we wish clearly to understand the structure of the membrane in those cells where the stratification is visible without its application, as it frequently happens that before it is applied, only a few thick layers are visible, and the acid demonstrates the presence of a great number of very delicate layers, for instance, in the thick-walled medullary cells of *Hoya carnosa*, of which fig. 11. Plate I. represents a fresh cell, and fig. 12 a part of the same swollen by the action of sulphuric acid.

When an acid acts strongly enough to render the stratification of a membrane distinct, it always causes it to swell more or less. Under these circumstances parenchymatous cells are extended in every direction; prosenchymatous cells and vessels, on the contrary, chiefly in thickness and breadth, and very slightly in length, as we also observe when they are moistened with water. The degree of distention, however, which a membrane undergoes in water, bears not the slightest relation to the tumefaction it exhibits in acid, for cellular membranes which swell up very much in water, for instance, the gelatinous cells situated beneath the epidermis, increase in size very little more in acid, while the wood- and liber-cells on which water exerts very slight influence, swell up exceedingly in acid, and the softer cells beneath the ligneous cells in the inner part of the annual ring, in a greater degree than the firmer ones situated more externally.

Very frequently the thick-walled wood- and liber-cells which have not been treated with acid, exhibit alternate broader and darker, narrower and paler layers; for instance, the liber-cells of *Cocos botryophora* (fig. 8. Plate I.), and in a less marked degree the liber-cells of *Calamus* (figs. 25, 26. Plate II.). This circumstance indicates a certain unconformity in the substance of the cell-wall, which is doubtless in consequence of a successive deposition of the layers. Another circumstance here presents itself to which at first one might be inclined to attach no importance, but to which I must call attention on account of the subsequent consideration of the wood-cells of Dicotyledons. The above-described layers are so stratified, that the most internal is always a thin and paler one. If we allow the liber-cells of *Cocos botryophora* to swell up in dilute sulphuric acid, the individual layers separate very

frequently in such a manner, that a thick one, and a thinner and somewhat paler one situated on its inner side, always remain attached together, which would make it appear that these two layers formed together a connected whole. The bright and the dark parts of each division show no perceptible difference in their behaviour to sulphuric acid and iodine, hence we are well entitled to consider them rather as slight modifications of the same membrane than as essentially distinct. On the other hand, slight distinctions occur in some cases between the different layers of the same cell in reference to their behaviour to iodine and sulphuric acid. Thus the innermost or even several of the more internal layers of the liber-cells of *Calamus* (see figs. 25, 26) are usually coloured of a darker yellow by iodine than the outer, and the inner swells somewhat more slowly than the outer layers in sulphuric acid; so likewise the inner layer of the parenchymatous cells of the stem of *Polypodium incanum* (fig. 18) is coloured a deeper yellow by iodine. If dilute sulphuric acid be allowed to act upon the cells treated with iodine, they will usually, though not always, take a blue colour at a certain stage of disintegration. If, then, as in *Calamus* and *Polypodium incanum*, the various layers exhibit a marked difference in respect to the rapidity with which they swell in sulphuric acid, the layer which first becomes swelled (consequently in this case the outer) will be coloured blue sooner than the inner, which remains yellow for some time, till the longer continued action of the acid renders it also blue. On this blue colouring, however, I can place no value whatever; it presents itself in all membranes swelling easily on the application of a weak acid, in all membranes swelling slowly by a strong sulphuric acid; and if two layers of the same cell show any difference in this respect, this is by no means a proof that we have different membranes before us, since even in the same layer differences of age in the cells suffice either to allow of or hinder the production of the blue colour on the application of acid. For instance, the primary membrane of all young organs is very readily coloured blue; the primary membrane of many full-grown cells is coloured blue, as in the spiral cells of *Melocactus*, and in the horny cells of very many plants; while the primary membrane of full-grown ligneous cells, as a rule, obstinately resists the action of sulphuric acid, and is not coloured blue; further, the secondary membrane of spiral vessels, dotted ducts,

coniferous woods, &c., is coloured blue only by the action of concentrated sulphuric acid, while the secondary membrane of most parenchymatous cells is coloured with the utmost ease. The blue colour, therefore, only shows the degree of laxity of the membrane of plants; it occurs in many vegetable cells, as in the cotyledon-cells of *Schotia* (fig. 17. Plate I.), on the simple application of iodine, in others it requires a weak acid, and in many cases, as in the wood of *Taxus*, it comes out only when the texture of the membrane has been wholly destroyed by a very strong acid; it may therefore frequently be a convenient means of enabling us to distinguish more readily two layers of a cell from each other, but it can never admit of any conclusion being drawn from it as to the primary or secondary nature of a membrane. As we have already seen, Hartig distinguishes the asthate from the ptychode and the eusthate, by the circumstance that the former acquires a blue colour by the action of iodine and sulphuric acid, while the other membranes remain yellow; this is totally false, as every one must find who extends his investigations over a greater number of plants.

A regular alternation of dark and pale layers, as above described, is not the condition which thick-walled cells usually exhibit, but in the majority of cases only one thin pale layer is to be remarked immediately bounding the cavity of the cell. This presents itself equally in thick-walled parenchymatous cells, as in the cells of the cotyledons of *Schotia speciosa* (fig. 17), and in prosenchymatous cells, especially in the ligneous cells of almost all our trees, which latter will be more specially considered hereafter. This inner pale layer appears more distinctly than would be the case but for the imperfection of our optical instruments, in consequence of a band of light which microscopes exhibit, on the employment of the high magnifying powers necessary in these investigations, at the edge and within the margin of all semi-opaque bodies. Since this band of light is a great obstacle in researches of this nature, I took every pains, by alterations of the illumination, by the employment of Dujardin's illuminating apparatus, &c., to remove it, but in vain. In the gelatinous cells lying under the epidermis of the stem of *Spinacia*, it will presently be shown how easily an illusion might arise from such a band of light, how, consequently, we might be led to think we could perceive, with great certainty, a peculiar membrane lining the cavity of the cell. In fig. 22.

Plate II. some of these cells are represented as they appear in a transverse section lying in water, and they apparently show an inner membrane quite distinctly. The application of a weak acid to the preparation, particularly if it is allowed to act for some time, say twenty-four hours, is a convenient mode of detecting this error; for, after the cell-membranes have acquired an equal transparency, and their stratification has become more distinct, it is perceived not merely that no inner membrane runs across the dots, but that the innermost layer terminates at them, and is similarly circumstanced to that of the innermost lamellæ of the secondary membrane of all other cells; and now the outer cellular membrane likewise appears, which in most cases had not previously been visible, and it is perceived that these cells, apparently so anomalous, are constructed quite according to the general rule (fig. 23. Plate II.).

The foregoing shows that the positive decision as to whether the cells are clothed by a special membrane or not, is opposed by no mean difficulties, since both optical illusion and a slight modification of the substance of the innermost cell-layers, quite possible in intermediate layers, may lead to the belief that we have found the supposed membrane. Perhaps further improvements of the microscope and other methods of investigation, may in time give rise to another opinion, but for the present I must decidedly assert, that in the majority of cells no inner membrane, distinct from the secondary layers, occurs. In this respect I believe that the medullary cells of *Taxodium distichum*, on which Hartig lays such great stress, form no exception. An inner brown coating, investing the secondary layer, does indeed occur in these cells, but that this is not a membrane belonging to the cell appears sufficiently clear from the facts that it is unequal in thickness, in many cells filling the whole cavity, and that in young cells starch granules are mixed up with it, &c.

Hartig believes that the secondary cell-layers are secreted by the ptychode; he does not say whether he considers the inner or the outer lamellæ the older. In my opinion, there can be no doubt that the exterior are the older; the mechanical relation of the different layers to each other, require positively the adoption of this opinion. In this respect two modifications occur. In the first, the layers of the secondary membrane do not run parallel to the outer walls of the cell, but exhibit an arched curve directed towards the interior of the cell, for instance in *Junger-*

mannia Taylori (fig. 2. Plate I.), *Schotia* (fig. 17). If in such cases we compare the young with the full-grown cell (viz. in *Jungermannia Taylori*, fig. 3 with fig. 2), we see clearly that in the former the narrowest layers alone, situated most externally, are yet in existence. The second modification occurs in the cases where the dots are small; in these the lamellæ of the secondary membrane run parallel to the outer wall of the cell, as in *Hoya carnosa* (fig. 11). In this case, indeed, the mechanical conditions of the layers present no grounds for declaring the inner to be the younger, but disregarding the analogy drawn from the foregoing case, the history of the development of these cells, in very many cases, does not allow the slightest doubt to be entertained but that here also the inner layers are the younger, since these cells frequently attain their full size in the condition of thin-walled cells, and then first commences the deposition of secondary layers within them.

In most cells no distinction is perceived between the different secondary layers, save the above described difference of colour. To this however there are some remarkable exceptions. The ligneous cells of some of the *Ficoideæ* I have examined exhibit a striking peculiarity in this respect, particularly part of the ligneous cells of *F. carica*, whose secondary membrane consists of two layers, of which the outer and firmer is coloured yellowish-brown by iodine, and the inner and softer violet (fig. 21. Plate II.). Exactly similar appearances are presented by the liber cells of a yearling shoot of *Rhus typhinum*.

While in this case the general layers are only distinguished by their different consistence, in other cases we find moreover a difference of structure. This occurs, for instance, in many plants in the cells of the seed membrane and the achenium containing a spiral fibre and swelling in water, in which three layers are generally to be distinguished, the primary outer membrane, a mucilaginous layer swelling in water, and the spiral fibre. The last may lie within the mucilaginous layer, as in *Collomia*, *Senecio vulgaris*, &c., or as in *Ruellia strepens* (fig. 32), surround the mucilaginous layer and adhere to the outer membrane. The mucilaginous layers of these cells are by no means to be considered as unorganized mucilage, for in certain cases, as in *Ruellia*, they appear to be composed of distinct superposed lamellæ.

In my opinion the ligneous cells of *Taxus* and the allied formations also belong to this division of cells, having two distinct

secondary layers. Several years since, indeed, I described* the fibres in the ligneous cells of *Taxus* as a peculiar cell-membrane, since the spiral course which they take in the cells of some trees is wound in a direction opposite to that of the greatest breadth of the canals of the dots. Hartig apparently founded his theory of the ptychode chiefly upon the structure of the wood of *Taxus*, and differs from previous phytotomists, principally in the circumstance that he assumes that the spiral fibres are not isolated in the interior of the ligneous cells, but connected together by a membrane, or rather are nothing else than inwardly projecting folds of this membrane (the ptychode). I examined the wood of *Taxus baccata* and *cuspidata*, *Torreya taxifolia* (fig. 10) and *nucifera*, with the application of sulphuric acid, in reference to these assertions, and agree perfectly with Hartig as to the presence of an inner membrane closely connected with the spiral fibres; whether the fibres owe their origin to a folding inwards of this membrane, as quite appears to be the case when the cellular membrane is half-swollen in sulphuric acid, or whether they are mere thickenings of it, I will not yet venture to decide, as my microscope does not suffice for an accurate investigation of these points. The accuracy of the further assertion of Hartig, that the canals of the dots are clothed by a continuation of this membrane, may also hardly be doubted, since we see a clearly defined band of light, appearing to proceed from an immediate continuation of that membrane, running through the canal of the dot as far as its outer end, but the precise determination of the relation which this appendage bears to the surrounding parts is also impossible with my microscopes. That the lenticular cavity which lies between two dots is clothed by a continuation of the outer cellular membrane, and is shut off from the canals of the dots, may be seen most distinctly, and I do not hesitate to declare the representation given by Hartig, that the inner cellular membrane passes through one of the dots into the cavity and lines it, to be wholly erroneous; but to make out whether the inner membrane ends in the form of a blind sac at the bottom of the canal of the dot, or, as in general, attaches itself to the external membrane, requires better microscopes than we possess at present.

That we should distinguish this inner membrane from the external secondary membranes, as a peculiar layer, sufficient grounds exist in its distinct spiral structure, in the variable

* *Dissertation über den Bau der vegetab. Zellmembran*, p. 26.

direction of its spiral, and in its continuation through the canals of the dots; but in my opinion there is not the slightest reason for placing it, with Hartig, in direct opposition to the secondary layers and regarding it as the primary membrane to which all the others owe their origin. No such extraordinary importance should be attached to the deviations in its structure from that of the outer secondary layers, for these differences are not nearly so significant as those we find between the different secondary layers in many other cells, especially in the spiral cells of the seeds of *Ruellia*, &c. Hartig's view could solely be deduced from the history of the development of these cells, but he does not appear to have traced this, neither would it favour his theory, for no spiral membrane is found in young cells. I myself prematurely hazarded a conjecture that it makes its appearance earlier than the outer secondary layers in the young cells. I must retract this in consequence of more recent observations, from which it appears to be the last formed membrane.

An equally striking distinction occurs between the outer and inner secondary layers in the cells of the wood of *Pinus sylvestris*, and still more strongly marked in the wood of *Taxodium distichum*. If a transverse section of the latter is allowed to swell in sulphuric acid (figs. 29, 34. Plate II.), the secondary membrane appears to be composed of two layers. The outer layer is thin, homogeneous, and the canals of the dots have a roundish form; the inner layer, on the other hand, is split into many lamellæ, which are perpendicular to the outer layer, and run in a spiral direction through the cell. The canals of the dots in this inner layer are formed by the mutual retraction of two such lamellæ, and consequently present the appearance of narrow oblique clefts (fig. 31). This layer appears perfectly homogeneous (fig. 30) before it swells in acid, and a multitude of delicate spiral furrows are seen to traverse it, only when it is examined from the cavity of the cell. Even during the tumefaction the division between the contiguous lamellæ is invisible, but the inner margin appears bordered by a band of light which seems to indicate the existence of an inner membrane; on complete distention however no trace of this is seen. The spiral striation of the inner cell-wall structure of *Pinus sylvestris* was one of the chief grounds on which Meyen founded his theory, that the cell-wall was formed by the growing together of distinct fibres. The presence of distinctly separated lamellæ in the tu-

mefied cellular membrane might be taken as an evidence of the correctness of this theory; but, on the other hand, this disruption into lamellæ may also be considered as a dissolution of a hitherto coherent membrane of a distinctly fibrous structure. I believe the history of the development is in favour of the latter view, at least I have never been able to see fibres in the interior of the cells of *Pinus*, during the progress of their growth, which were not yet attached to a membrane. Be this as it may, the firm coherence which the outer layer of secondary membrane of the said plants retains in acid, shows as clearly as does the roundish form of the canals of the dots in this layer, that it possesses a structure different from the inner layer. We have here therefore a relation similar to that in *Taxus*, with the difference only that the spiral layer is here uncommonly developed, while in *Taxus* it is extremely thin, and as respects the outer layer, the contrary is the case. It is certain that in *Pinus* the outer layer is developed before the inner.

The wood of other Coniferæ I have examined does not exhibit such a striking distinction between the outer and inner layer of the secondary membrane; one difference however may be perceived, which is, that the cavity of the cell is surrounded by a band of light with tolerably distinct outlines. That this band is not occasioned by an optical illusion is evident, from the innermost layer of the cell swelling much less strongly than the outer in sulphuric acid, in consequence of which it tears away in one or more places (fig. 13), upon which the parts of the outer layer corresponding to the torn places expand very much in breadth; or the outer membrane detaches itself from the inner in particular places on account of the more considerable swelling (fig. 14), for example in *Juniperus virginiana*, *Sabina*, *Abies pectinata*, *Gingko biloba*. No peculiarity of structure is to be perceived in this inner layer.

The presence of an inner layer is not peculiar to the ligneous cells of Coniferæ, but occurs equally in the prosenchymatous cells of Dicotyledons, and the same modifications we found in *Taxus* and *Torreya*, and in *Juniperus*, *Ginkgo*, &c., are repeated in these. The latter is the usual modification in Dicotyledons, as instances of which I may name *Quercus Robur*, *Piscidia Erythrina* (fig. 28, before tumefaction; fig. 27, the same swollen), *Myrtus acris*, *Cobæa scandens*, *Aralia arborea*, *Laurus nobilis*, which plants however I do not bring forward as instances in

which the inner layer is very distinctly developed, but because it was accidentally in them that I ratified my previous observations of this appearance, before writing the present remarks. It is far more uncommon for the inner layer to be coated by spiral fibres, as occurs in *Viburnum Lantana* (fig. 15, 16), *Euonymus atropurpureus*, *Sambucus nigra*.

Passing to the outer cellular membrane, we must first consider a remark of Hartig's (founded indeed on a perfectly correct observation), namely the assertion that the outer membrane of contiguous cells is to be regarded as a layer common to both, without any line of separation in the middle, and that therefore phytotomical drawings hitherto published which exhibit such a line of separation are incorrect. This assertion is fully warranted as far as relates to the cells and vessels of Phanerogamia, but in the Algæ, in which a more or less abundant intercellular substance is present, the outer membrane of each cell is separated from that of the neighbouring cell by a layer of intercellular substance (fig. 19). Is it probable, as Hartig believes, that the outer membrane lying between two cells is common to both, or does it appear to us merely as a simple membrane because the line of separation escapes our optical instruments? This question is difficult of solution by the direct observation of Phanerogamia, but it cannot be doubted that the membrane forms no homogeneous layer between the contiguous cells, as Hartig assumes, but that they are either composed of two membranes intimately coherent, as would appear from the cells of the Algæ, or it is at least possible that a division into two membranes takes place in consequence of organic processes (which really has been effected by nature in many cases); in favour of which view may be instanced the separation of the cells of *Zygnema*, and the formation of intercellular passages in Phanerogamia. That this membrane is the youngest, and is separated in a fluid state from the already existing inner cell-membranes, as Hartig assumes, is wholly improbable, from the firm coherence which the cells exhibit at every period of their existence. Leaving out of the question that not one fact is known which speaks in favour of this view (for Hartig's assertion that the outer membrane is present only in the intercellular passages, in many gelatinous cells, is founded on imperfect observation), a complete proof that the outer cellular membrane is not the youngest but the oldest, exists principally in two circumstances; in the first

place, as has been mentioned above, the latter view is the only one compatible with the deposition of the secondary layers in the cells of *Jungermannia Taylori*, *Schotia speciosa*, &c.; secondly, we can convince ourselves by the examination of the cambium layer of Dicotyledons, that the thin wall-structure of the elementary organ of this layer is an immediate continuation of the reticulation which forms the primary membranes in the older portion of the wood. The investigation of this point is frequently far more difficult than it would at first appear, but in *Pinus sylvestris* any one may convince himself in the most positive manner, as in this the cambium cells resist the action of sulphuric acid (which was not the case with any other of the plants I examined), while the secondary layer, both in the liber- and ligneous-cells, swells strongly in acid, which renders the above-mentioned connexion and similarity of their outer membrane with the membranes of the cells lying in the cambium layer distinctly evident.

If the representation of the process of cell-multiplication which I have above given be in accordance with nature, the septum which is developed between two primordial utricles, and subsequently divides the simple cell into two, would come into immediate connexion with the primary membrane of these cells (since the process of increase in cells usually takes place at a period when no secondary membrane has yet been deposited), and in this way the connexion of all primary membranes in the form of a web would be more simply explained. Whether these septa consist of a single homogeneous layer, or of two lamellæ, is, from their great delicacy, not to be determined with our present microscopes.

If we assume that the septum consists of two layers, it will indeed be most natural to suppose that it is formed by a circular folding-in of the primary cellular membrane; in this way would be explicable how each cell possesses its own proper membrane, and how the intercellular passages and the cavities between the dots are formed by the mere retraction of the contiguous cellular membranes. If we assume, on the contrary, that the primary membrane is common to two cells, and consequently that the newly-formed septum is likewise simple, we must admit that these cellular membranes subsequently undergo an internal change which renders possible a separation into two layers, for the purpose of forming intercellular passages and cavities of the dots.

I have never succeeded in separating the primary membrane into two layers by the application of acid, in the Phanerogamia, even by boiling in nitric acid. It swells somewhat in the acid. In gelatinous or horn-like cells, it generally extends in breadth in the same proportion as the secondary layers; in lignified cells, on the contrary, its expansion in breadth is usually very slight, so that it is consequently torn by the violent swelling of the secondary layers. Its increase of thickness is never remarkable; in some cases where this resulted to a greater extent than usual, it showed that the primary membrane consisted of many superposed layers; this was especially the case in the liber-cells of *Cocos botryophora* and in the parenchymatous cells of the stem of *Polypodium incanum*. An outer layer presented itself in both, which in *Cocos* (fig. 9) met and came in contact at one point, at the corner of the cells, with the corner of the corresponding layers of the other cell-walls; in *Polypodium* (fig. 33), on the contrary, a triangular interval was left, either empty or filled with intercellular substance. Joining these decided facts concerning the stratification of primary membrane with the circumstance that the septa which form in the cambium layer are usually perceptibly thinner than the primary membranes of full-grown cells, and that a similar thickening of the primary membrane is visible on comparing an old and young leaf in mosses (figs. 2, 3), we must conclude that the primary membrane increases in thickness during the development of the cell, and that this, analogous to the increase of thickness of secondary membrane, consists not in an extension in thickness of the original membrane, but rather in the deposition of lamellæ upon it.

EXPLANATION OF THE PLATES.

PLATE I.

Fig. 1. Transverse section of the cambium layer of *Pinus sylvestris*. The primordial utricles have separated from the cell-wall in consequence of the action of spirit of wine, and are coloured by iodine.

Fig. 2. Cell of a full-grown leaf of *Jungermannia Taylori*. The primordial utricle is detached from the cell-wall.

Fig. 3. Cell of a young leaf of *Jungermannia Taylori*.

Fig. 4. Cell of a leaf of *Vallisneria spiralis*. The primordial utricle is coloured by iodine.

Fig. 5. Medullary cell of *Asclepias syriaca*. The primordial utricle is in the act of dissolution.

Fig. 6. Bark cells of *Euphorbia canariensis*. The primordial utricles are coloured by iodine.

Fig. 7. Cambium cells of *Sambucus Ebulus*, with primordial utricles.

Fig. 8. Liber-cell of *Cocos botryophora*, coloured by iodine.

Fig. 9. Primary cellular membrane of the liber of *Cocos botryophora*, swelled in sulphuric acid.

Fig. 10. Longitudinal section of the wood of *Torreya taxifolia*, half-swollen in sulphuric acid.

Fig. 11. Dotted medullary cell of *Hoya carnosa*.

Fig. 12. A piece of the last swollen in sulphuric acid; in consequence of the tumefaction, the canal of the dot running through the centre has lost its sharp outline.

Figs. 13 and 14. Ligneous cells of *Juniperus virginiana*, swollen in sulphuric acid. The primary membrane is torn by the swollen secondary membranes and is not represented.

Figs. 15 and 16. Ligneous cells of *Viburnum Lantana*.

Fig. 17. Cells from the cotyledon of *Schotia speciosa*, coloured by iodine.

Plate II.

Fig. 18. Transverse section of the parenchymatous cells of the stem of *Polypodium incanum*, coloured by iodine.

Fig. 19. Transverse section of some cells of *Furcellaria fastigiata*. The primordial utricle lying in one of them is detached from the cell-wall.

Fig. 20. Transverse section of a ligneous cell of *Juniperus virginiana*.

Fig. 21. Transverse section of ligneous cells of *Ficus Carica*, coloured by iodine.

Fig. 22. Gelatinous cells lying beneath the epidermis of the stem of *Spinacia oleracea*.

Fig. 23. Cells, as in fig. 22, treated with hydrochloric acid.

Fig. 24. Ligneous cells from a cane (*Calamus* —— ?), coloured by iodine.

Figs. 25 and 26. Liber-cells of *Calamus*, coloured by iodine.

Fig. 27. The secondary layers of a ligneous cell of *Piscidia Erythrina*, swollen in sulphuric acid.

Fig. 28. A ligneous cell of *Piscidia Erythrina*, in its natural state.

Fig. 29. Transverse section of a ligneous cell of *Taxodium distichum*, swollen in sulphuric acid. The primary membrane has become detached and is not represented.

Fig. 30. Ligneous cell of *Taxodium distichum*, in its natural condition.

Fig. 31. Longitudinal section of a ligneous cell of *Taxodium distichum*.

Fig. 32. Hair of the seed-membrane of *Ruellia strepens*, treated with iodine. The mucilaginous cellular layers with the primordial utricle project from the external membrane in consequence of the swelling in water.

Fig. 33. Primary membrane of the cells of *Polypodium incanum* (fig. 18), swollen in sulphuric acid.

Fig. 34. A portion of the secondary cell-layers of *Taxodium distichum*, treated with sulphuric acid.

Article V.

A Description of the Chalk Formation of Northern Germany.*
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[The author states that all the drawings of his plates were executed and lithographed by himself; and that great attention was given to the references to the localities whence the specimens described were obtained.]

HAVING examined and described the several organic remains of the chalk formation in Northern Germany, it is my intention at present to give a brief description of the geognostic relations of that series of strata. To attain this object, the several individual deposits and mountain ranges of the chalk might be described separately, and the peculiarities of each might be enumerated in apposition; but in this way it would be impossible to avoid innumerable repetitions; and I have thought it more advantageous to trace the several divisions of the chalk series through the whole of Northern Germany (the limits of which have been passed in this treatise, in the cases only of Maestricht and Heligoland),—and to add, at the conclusion, a short account of the composition and stratigraphical relations of each separate range.

I have in the present instance, as formerly with respect to the oolitic groups, compared the relations of the chalk observed in Northern Germany, principally with those which are exhibited in England, because it is only in that country that complete descriptions of them exist, and that the German chalk formation obviously more nearly resembles that of England than of any other region. But I have not on this account submitted the relations of this country to any unfounded limitation, as the evidence afforded by the fossils will prove.

The Weald-clay formation, which has hitherto been described by other writers in connexion with the chalk, I regard as more nearly allied to the deposits of the Jura, from the various genera of fish and reptiles which occur in it. I have therefore in the

* Being the Appendix to a work, entitled "Die Versteinerung des Norddeutschen Kreidegebirges," ('The Fossils of the North German Chalk Formation,') published at Hanover, in two parts, 1840 and 1842:—Quarto, 145 pages, with 16 lithographic plates. Translated by Mr. William Francis, and revised by Dr. Fitton.

present treatise passed over this formation in silence; and may refer to my earlier investigations respecting it*.

Premising that two divisions only of the cretaceous series,—an upper calcareous, and an inferior or sandy division,—have hitherto been distinguished in Germany, we shall now consider more closely the several deposits, beginning with the most recent.

I. THE UPPER CHALK:—Chalk. [Die obere kreide—*Craie.*]

In those districts where the chalk formation was first recognised and described as an independent group, it was its upper member, the white chalk, which, from its dazzling colour, from the purity of the stone and from the alternating seams of flint, must have attracted the special attention of the geologist. It is everywhere readily recognised by these mineralogical characters; and from it all the deposits older than the Eocene and younger than the Weald-clay, have been called the "chalk formation" (*formation crétacée*:—kreide-gebirge).

It has been observed in England that seams of flint occur only in the upper portion of the white chalk, and that the inferior layers of chalk gradually lose their purity and colour; on this account the chalk with flints has been distinguished from that without flints; a distinction which, we shall find, is in some measure justified by the palæontological characters.

Hitherto the white chalk only has been considered as the upper member of the chalk formation; and several deposits which present a different mineralogical character have been considered, owing to a neglect of their organic contents, some as more recent, others as older, which nevertheless the fossils which they contain decidedly prove to be of the same age. This remark applies especially to the formation of Petersberg near Maestricht, with the heights around Falconberg (Fauquemont); and to several sandy marls, sandstones and conglomerates which occur to the north of the Hartz mountains, and in Silesia: these several formations we shall now describe singly and more in detail.

1. *Upper Chalk*:—Chalk with flints—flinty chalk—part of the white chalk. [Obere weisse kreide:—part of the *Craie blanche.*]

This consists of a regularly stratified deposit, 500 feet in thick-

* "Fossils of the Oolitic Formation in the North of Germany," with 10 plates. Hanover, 4to, 1836.

ness, of pure white carbonate of lime, inclosing seams and bands of flints in intermediate layers, and in oblique or vertical fissures.

The carbonate of lime is compact, or has an earthy fracture; adheres more or less to the tongue; is generally of a pure white colour; sometimes it is soft, as for instance in the writing chalk, at other times somewhat harder; and it is so free from foreign constituents that scarcely 0·006 silica is found in it. This in some cases is accompanied by a little iron, which imparts to it a grayish colour. The specific gravity is about 2·34.

The single layers are from 1 to 4 feet in thickness, and are generally much rifted.

Numerous seams of flints, from a few inches to some feet in thickness, alternate with the calcareous beds. The flints have a specific gravity of 2·594, and contain, according to Klaproth's analysis,—

Silica	0·98
Carbonate of lime	0·005
Alumina	0·0025
Oxide of iron (eisen oxyd)	0·0025
Water	0·01

In the interior, the colour of the flints varies between gray and black; they possess a conchoidal fracture and a faint lustre, are translucent at the edges, and sometimes include cavities partially filled with chalcedony and crystals of pure quartz; by exposure to the air their colour gradually becomes yellowish; and in the fire whitish and quite opake. Very frequently minute, well-preserved corals are found in them, which perhaps may alone have effected the separation of the acid of silica*.

The flints form roundish irregular nodules, frequently flattened, and varying in size from that of a fist to several feet in diameter: they lie close together, seldom however in contact, and are commonly surrounded by the chalk; their surface, which consists of a combination of lime and silica, is whitish, rough and harsh to the touch. These flints frequently form only horizontal seams, but sometimes numerous ranges of them (schnüre) are met with, traversing the other strata in a perpendicular or inclined direction.

Of other minerals there occur calcareous spar, chalcedony, crystals of quartz, and iron pyrites. The calcareous spar fre-

* Welche die aussonderung der kieselsäure allein bewerkt haben (Orig.).

quently clothes the sides of fissures; while the iron pyrites forms globular, racemose, spindle-shaped or very irregular masses, wholly inclosed in the chalk.

In Germany the upper white chalk is one of the rarest formations, and makes its appearance on the isle of Rugen and in New Pomerania: on the isle of Jasmund (near the fishing village of Sassnitz, as far as the estate Ranzow, further to the north) it forms perpendicular cliffs, which at the Stubbenkammer attain a height of 400 feet. This formation is likewise exposed to view at some detached points on the coast of the peninsula Wittow, of the island Hiddensen, and of Granitz in Rugen, as well as at several places in the interior of the island; for instance near Altencamp and Presche. In New Pomerania the localities are Quitzen, Gustebin, and Wassin, and Stengow on the island Wolin; with respect to these places, however, it is doubtful whether in some cases it may not be the lower white chalk which is exposed.

2. *Maestricht Limestone.* [Maestricht kalk.]

The hill of Petersberg near Maestricht, which is several hundred feet high, consists of a bright yellow, sandy, calcareous mass, in the lower portion of which are from ten to fifteen seams of black flints at a distance of about two feet from one another. The stone is generally friable and sometimes separates in great blocks; it is a very pure limestone, and contains, according to my analysis,—

Clay and sand	0·0050
Oxide of iron (eisen oxyd) . . .	0·0025
Alumina	0·0025
Carbonate of lime	0·9650
Carbonate of magnesia	0·0100
Water	0·0150

The lower layers gradually become whiter, but nevertheless retain their peculiar sandy texture, so that I could not find in the valley of the Meuse near Maestricht, even opposite to Visé, any stone which possessed the mineralogical character either of the upper or lower white chalk of England.

This formation occurs with precisely similar characters at Falconberg (Fauquemont), at a short distance from Maestricht; where, at the foot of the castle bearing the same name, are si-

tuated the entrances to labyrinthine quarries, close to which numerous fossils are found.

Several geologists have referred to this division of the chalk the strata which constitute the upper portion of the Louisberg (Lausberg) near Aix la Chapelle, and especially the stratum, about four feet in thickness, of yellowish sandy limestone, with the layer beneath it from 1 to 2 feet in depth, consisting of flints, hornstone and limestone. This latter is said to contain a large number of the Maestricht fossils; unfortunately I have not been able to discover even a single one. We shall enter into more detail on this subject in the following section.

It has hitherto been generally admitted that the Maestricht formation is more recent than the upper white chalk; and this deposit has even been represented as a connecting member between the chalk formation and the tertiary deposits, but I think without reason, and I cannot but consider it as a true equivalent to the English white chalk with flints.

There occur, it is true, among the fossils of Maestricht and Falconberg, several which appear to be absent in the upper chalk of other districts, for instance, *Astrea*, *Diploctenium*, *Orbitolites*, *Crassatella latissima*, &c.; but hitherto we have not succeeded in detecting even a single species which had been found in other places along with any tertiary species; while, as regards the characteristic forms of the upper chalk,—such as *Mososaurus Hofmanni*, *Callianassa Faujasii*, *Belemnites mucronatus*, *Apiocrinites ellipticus*, and the numerous small corals,—they nearly all occur at Maestricht and Falconberg. Even if it should be proved that this formation is actually underlaid (unterhaüft), above Maestricht and at Henri Chapelle, by a pure white chalk, the latter will doubtless prove to be the *lower chalk* (*"chalk without flints"* of the English).

It will not appear surprising that some fossils should occur at Maestricht which are absent in other districts, if we take into consideration the peculiar mineralogical nature of the Maestricht stone, which was certainly produced by circumstances which did not exist contemporaneously on the English coast. But a difference in the mineralogical properties of the rock would not alone justify our inferring a difference in the age of the deposit, even if the upper *chalk marl*, which we shall presently consider, were allowed to be an equivalent of the *upper chalk* itself.

3. *Upper White Chalk Marl.* [Oberer kreidemergel.]

At a short distance from the northern foot of the Deister, about two hours' walk (zuei stunden) from Hanover, and in the neighbourhood of the village of Gehrden, is situated a hill about 100 feet in height, which is laid open towards the western side near the windmill, and on the north-western declivity, by quarries. The lower masses of stone consist of beds, from 4 to 10 feet in thickness, of a grayish sandstone; on which rest some sandy marls about 20 feet in thickness, which are more or less compact, in some places slaty, and alternately of a yellowish-gray and bluish-gray colour. The lower beds are rifted into large square masses, while the upper layers exhibit no remarkable separations; the latter inclose in some places so great a number of minute, broken and worn corals, that the stone acquires the appearance of a coarsely granular conglomerate; and all the strata contain numerous fossils.

This upper chalk-marl presents, near Halberstadt, a somewhat different appearance. On proceeding southward from that place to the Spiegelberg, we first observe, on the high road, the gray chalk-marl (plæner); very soon, however, a sandy formation appears, and at the foot of the mountain a coarse conglomerate, of quartz, with a blackish or brownish, strongly ferruginous, siliceous cement; in this the granules of quartz are rounded, become gradually smaller, the proportion of iron in the connecting medium decreases; and, gradually, the conglomerate passes into a fine-grained yellowish or whitish, slightly-stratified sandstone, separated into large blocks, which is very much disposed to decay, forms some isolated rocks, and may perhaps attain a thickness of 150 to 200 feet. This latter rock forms a broad plateau or a flat trough, which extends southwards as far as Munchhof, near Quedlinburg, where it again rests upon the gray chalk-marl (plæner), in beds inclining toward the north, and has a longitudinal extension of several miles in the direction of the stratification.

A third detached appearance of a portion of the upper chalk marl occurs near Goslar on the northern border of the Hartz, the Sudmerberg of that neighbourhood, belonging to this formation; at the southern foot of this hill, in the bed of the Abezucht, there succeeds to the gray chalk-marl (plæner), into which it gradually passes, a sandy marl, on which rests the remaining mass of the hill, consisting of a conglomerate of quartz with an

ochre yellow, calcareous, sometimes crystalline matrix. This mass is separated into considerable beds, which here also form a flat trough (mulde), with beds on the south inclining northward, while towards the north they have a southern inclination. This deposit has been considered by Boué as belonging to Jurassic, by Këferstein to the tertiary period, and was first referred to the chalk by Hausmann.

We find also some members of the chalk formation near Wernigerode, where, on the Schlossberg and Galgenberg we meet with some conglomerated, tolerably compact sandstones in beds from 1 to 3 feet thick, which are separated from each other by softer masses of marl. The same rock is likewise exposed near Altenrode, where, not unfrequently, small nests of pitch-coal occur in it.

The masses of the Plattenberg near Blankenburg also belong to this division, consisting sometimes of a compact slaty, yellowish or brownish sandstone, frequently separated into globular masses of 1 to 2 inches in diameter; sometimes of a scaly, more dense and compact sandstone, passing into a coarse conglomerate.

The Salzberg near Quedlinburg consists of the very same rocks as the hill above described near Gehrden; and we find the very same fossils at both places.

There can be little doubt that the adjacent Teufelsmauer is of a similar age throughout its whole extent; it is formed of a compact sandstone, with a siliceous basis, frequently separable into flags; and on the northern declivity we meet among the fossils with an *Inoceramus*, calling to mind *I. Cripsii*, *Pygorhynchus rostratus*, and *Credneriæ*, which are however likewise frequent at Plattenberg.

From the absence of distinct fossils it is far more difficult to determine the relations of this deposit in the so-called "Saxon-Switzerland;" those considerable masses of sandstone, which have there an almost horizontal stratification, are separated in the declivities of several sections of the valleys into upper and lower, by a distinctly stratified sandy marl, sometimes of a green colour, which is perfectly similar in its mineralogical character to the streaked marls (flammen-mergel*) of our neighbourhood.

* *Flammen*, besides its original signification, "to flame," is said in the Dictionaries to be applied to the process of watering silks, &c., by which an appearance is produced of waving (flame-like?) stripes or streaks.—TRANS.

The lower masses here contain *Cardium Hillanum, Pecten equicostatus, Pinna decussata,* and therefore evidently belong to the quader sandstone (lower greensand); while the upper, likewise a very massive sandstone, has never been found to contain those fossils, but, on the contrary, *Terebratula alata,*—a fossil which is peculiar to the upper chalk; and we therefore consider all those masses of sandstone in Saxony, which rest upon the marly mass here described, to be equivalent to the *white chalk* with flints. We have distinctly recognised this sandstone above the marl, so abundant in springs, close to Pirna, in the valley of the Gottlaube, near Rottwernsdorf and Kritzschwitz, and at several places at the foot of the Schneeberg. The Saxon geologists look upon it as the English gault; but the characters of the stone oppose this view; and the stratigraphical relations are not in favour of it, since the upper greensand (for which they take the pure sandstones above the marl) never attain such a height, never contain *Terebratula alata,* and almost always appear to be very argillaceous, and to abound in lime and iron. Hitherto it has been impossible to determine, in the collections of fossils of that neighbourhood, which species have been found in the upper and which in the lower of these beds of marl; but whenever this can be ascertained, it will probably be easy to decide which of the two views is the more correct.

Still further towards the east a similar equivalent to the white chalk with flints occurs, in the county Glatz, near Kieslingswalde, where it appears as a dark gray calcareous sandstone, abounding in minute laminæ of mica, and passing, by the reception of small pebbles of flint, into a true conglomerate; numerous fossils occur in it, partly as fragments, but some very well preserved.

Quite at the western extremity of our district we meet with the upper chalk-marl, near Aix la Chapelle at Louisberg, and in the so-called Aachener Wald. The following section is exposed at the first of these places.

SECTION AT THE LOUISBERG NEAR AIX LA CHAPELLE.

Feet*.

1. A calcareous yellow sand containing *Mososaurus,* fishes' teeth, *Belemnites mucronatus*; which Hausmann has justly compared to the formation at Maestricht . 4

* The German measures probably employed in the paper are so little different from those of England, that it has not been thought necessary to con-

	Feet.
2. Hornstone and flints, in nodules, or in thin seams .	2
3. Yellowish calcareous sand, frequently united into a loose sandstone	20
4. Fine-grained, ochre-yellow, calcareous sandstone, with silicate of iron	2
5. A considerable bed of sand, with nodules and pipes of a sandstone united by oxide of iron	20
6. A gray soft schistose clay	1
7. A white calcareous sand, sometimes slightly agglutinated	

The sandstone referred to under No. 4, which still contains 42 per cent. of carbonate of lime, abounds in fossils, among which we find the following:—

Pecten arcuatus.	Rostellaria Parkinsonii.
Pholadomya caudata.	Turritella nodosa.
Voluta ambigua.	Cucullæa glabra.
Auricula incrassata.	Baculites anceps.

From the absence of minute corals, it remains doubtful whether the neighbourhood of Dülmen in Westphalia does not likewise belong to this formation; it constitutes a low plateau extending towards Coësfeld, the rock of which is exposed in several quarries, especially in Voigt, in the Duchy, and Hinderking. At all these places we observe under the soil, and in beds of loam (lehm-ablagerung), a loose sandstone from 1 to $1\frac{1}{2}$ foot in thickness, which soon crumbles by exposure to the air, and which contains numerous fossils; this is succeeded by a fine-grained, loose, mostly bluish sand, from 5 to 6 feet in depth; and then follows a compact calcareous sandstone, of a dirty-gray to a blackish-blue colour arising from carbonaceous matter, which is employed in mending the roads, and contains but very few fossils; beneath this there is another mass of loose sand, which according to some borings rests upon sandstone: all the layers have a nearly horizontal position.

The following fossils appear to be characteristic of those portions of the upper chalk in North Germany, which are parallel

vert them; nor is it quite certain what standard has been employed by the author. The *Hamburgh* foot is to English as 0·958 to 1·000. The Cologne, or Rhinland foot, as 1·030 to 1·000. The Neufchatel, or Prussian foot, as 0·984 to 1·000. (*Nautical Magazine*, 1840.) The German foot, like the English, is divided into twelve inches (zoll.); and six feet make a lachter, or fathom.—Trans.

to the English chalk with flints,—especially of the upper chalk, the Maestricht beds, and the upper white chalk marl :—

Credneria?
Heteropora dichotoma.
Chrysaora pulchella.
Pustilopora verticillata.
Apiocrinites ellipticus.
Marsupites Milleri.
Terebratula Defrancii.
Ostrea sulcata.
Pecten septemplicatus.
Pecten Faujasii.
Exogyra laciniata.
Pholadomya caudata.
Pectunculus lens.
Trigonia alæformis.
Crassatella arcacea.
Goniomya consignata.
Turritella nodosa.
Turritella alternans.
Belemnites mucronatus.
Ammonites bidorsatus.
Callianassa Faujasii.
Serpula filosa.
Mososaurus Hofmanni.

It is possible that some of these species may yet be met with in the lower chalk also, but the majority will certainly remain exclusively peculiar to the upper chalk. The large number of minute corals is in general very striking in the latter, and also the rarity of marine sponges, which are so generally distributed in very large numbers in the lower chalk. The minute corals are absent at Aix la Chapelle, Dülmen, Blankenburg, and Kieslingswald ; but there remain other fossils in sufficient number to prove the affinity of the deposits there, to that of other places. As far as I am aware, the fossils of the upper and of the lower chalk have hitherto never been enumerated separately either in England or in France, and it is therefore impossible to determine with certainty how far these countries agree in this respect with the north of Germany.

We may observe moreover, that the whole of the sandstones and marls which occur in the south of Sweden, for instance at Köping, Kjugestrand, Balsberg, Yngsjö, and Mörby, probably belong to the chalk, and are of the same age as the rocks above described. Formerly these were generally referred to the greensand and quader sandstone. Seams of coal occur in them at some points in Sweden, and likewise in the neighbourhood of Quedlinburg; at which place many years ago some mining operations was carried on in search of minerals.

II. The Lower Chalk. [Die untere kreide.]

1. *Lower white Chalk*:—Chalk without flints. [Untere weisse kreide.]

This differs from the preceding deposits, principally in a mineralogical respect, in the absence of flints, a somewhat greater hardness, and a darker grayish colour. The individual strata are very much divided by fissures, have little thickness, and sometimes are separated by seams of light-coloured marl: the thickness may be estimated at about 200 feet.

Such is the character of this formation as it occurs in England, in France, and also in the north of Germany. In the isle of Rugen it probably underlies the upper chalk. It certainly occurs at Schwicheldt and Theidensen near Peine, where the rock is obtained in numerous quarries, and is employed in marling the land; and to the north-west of the village Oberg, between Hildesheim and Brunswick. At those spots about 15 feet of the rock are exposed to view; and it will probably be found in the whole district close beneath the surface.

To this division likewise belongs the white loose clayey-chalk marl, which is excavated at some pits on the northern declivity of the Linden Berg, and is employed in purifying sugar; likewise the chalk deposit near Luneburg. It also crops out in the bed of the Lower Leine between Hanover and Limmer.

Probably of the same age, or a little older, is—

2. *The Lower White Chalk Marl*; [Der untere kreidemergel],—

which is in general a light gray-coloured limestone formation, with a greater amount of alumina and quartz.

The rock constituting the range of hills between Ilten and Ahlten near Hanover, comes nearest in character to the upper chalk. We find here yellowish white, somewhat sandy marl in thin layers at the top, but much thicker below, which generally becomes quite white soon after exposure to the atmosphere; the upper layers are in a mineralogical respect still very similar to those of Peine.

The deposit near Lemförde and Halden, to the north of Osnabruck, is already widely different; the somewhat extensive hill there, about 150 feet high, consists of layers from half a foot to 3 feet in thickness, of a yellowish-gray, light, finely porous, tolerably compact chalk marl with a close earthy rough fracture.

Numerous minute straight pores traverse the stone in all directions; they are finer than a hair, as much as three lines in length, and are probably the spaces out of which the spiculæ of Amorphozoa have been dissolved.

The stone afforded on analysis—

Water	0·080
Carbonate of lime	0·260
Silica	0·590
Oxide of iron	0·045
Alumina	0·025

It is obtained from numerous quarries for building.

At Osterfeld, a few miles from Essen, on the Ruhr, a group of strata perfectly similar to that above described is visible, but we are acquainted with it only by its fossils.

The sandy marls which form the ridge of hills situated to the north-east of, and close to Coesfeld in Westphalia, are distinguished from those above mentioned by a larger amount of sand, a light gray colour, and by a more strongly marked stratification and rifting (zerklüftung); they likewise contain numerous spiculæ of Amorphozoa (?), in general well preserved; and besides these, very minute blackish angular grains, which appear to be silicate of iron, but are so much inferior in quantity to the remaining mass that they have but a very slight influence on the colour of the stone; on the western declivity of the hill this rock is exposed in numerous but small quarries, and is used for building.

Whether the yellower and more sandy rock of the Baumberg close to Coesfeld, which is said to be connected with the above ridge, and is characterized by numerous and beautiful remains of fish, is of precisely the same age with that above mentioned, must be left undetermined, bad weather having prevented my examining that hill.

A lower chalk marl, like that of Coesfeld, occurs also at some points of the northern border of the Hartz mountains, for instance at Ilseburg and Stapelnburg, where it forms flat, rounded (gewölbte) hills, and appears as a gray sandy marl in thin strata with numerous fossils.

The lower chalk and the lower chalk marls appear to be parallel formations, and are probably more closely related, palæontologically, to the upper chalk than to the gray chalk (plæner); but it would be vain to search for sharply defined limits, either

above or downwards. It may appear surprising that no distinct superposition of the upper chalk upon the lower has been seen anywhere in our district, but this is without doubt owing to the former being found almost everywhere deposited horizontally and in ridges of low hills; at Sudmerberg near Goslar, for instance, the lower layers which contain numerous *Scyphiæ* and *Siphonia*, may perhaps be considered as actually equivalents to the lower chalk. We have nowhere met with the lower chalk to the east of the Hartz mountains.

The following fossils are widely distributed and confined to the lower chalk:—

Pleurostoma lacunosum.	Cœloptychium sulciferum.
... radiatum.	Avicula cœrulescens.
Scyphia Oeynhausii.	Arca furcifera.
... Murchisonii.	... tenuistriata.
... Coscinopora.	Pholadomya umbonata.
Cœloptychium agaricöides.	Delphinula tricarinata.
... lobatum.	Pyrula planulata.

The following species appear to be confined to the upper and lower chalk:—

Gryphæa vesicularis.	Baculites Faujasii.
Ostrea flabelliformis.	... anceps.
Lima semisulcata.	Crania Parisiensis.
Hamites intermedius.	... costata, &c.

If we add to these facts the scarcity of *Ammonites*, the occurrence of large variegated *Scaphites*, and the presence of two easily distinguishable *Belemnites*, it will seldom be difficult to determine, from the fossils, whether a sandy formation should be referred to the formations just mentioned, or to the still lower divisions of the chalk series which we are about to describe.

III. Gray Chalk Marl:—Gray Chalk*. [Der Plæner.—Kreide-mergel, Wald kalk, Binde kalk, Helmstein.—*Craie Tuffeau, craie grossière.*]

The gray chalk-marl (plæner) is described in England as a soft friable marl, light gray, passing into brown, frequently coloured by peroxide of iron, but which sometimes alternates with harder seams, and gradually passes downwards into the upper greensand.

* See note in the following page.

This description answers likewise for the plæner* of the North of Germany, where it appears generally as a more indurated chalky marl or limestone, seldom quite white, often somewhat grayish, sometimes reddish or greenish,—which is decidedly stratified, and much divided by fissures, and in the lowest strata gradually acquires more clay and silica, and oxide of iron, accompanied by a change of colour. Analysis gave

	For the white chalk marl (plæner) of the Kromsberg.	For the gray marl (plæner) from near Rethen.
Water	0·040	0·050
Carbonate of lime	0·865	0·855
Silica	0·055	0·060
Alumina	0·020	0·010
Oxide of iron (eisen oxyd)	0·020	0·020
Magnesia and oxide of manganese	0·000	0·005

The greatest thickness of this division of the chalk formation is estimated in England at 200 feet; but in several of the German localities, *e. g.* at Langelsheim in the Hartz and at Alfeld, it increases to 1000 feet, and even more.

The most westerly deposit of the plæner is observed at Essen on the Ruhr; where, especially in the neighbourhood of the town, it overlies the Hils-conglomerate in inconsiderable thickness; from this place it may be traced, by Bochum, to Padeborn, thence by Bielefeld, Iburg, to Grass near Ahaus. At Bochum it consists of a soft yellowish-white to bluish-gray chalk marl, containing *Inoceramus mytilöides* and *Ammonites varians*. To the east it becomes harder, and gradually acquires the appearance of the ordinary (plæner) gray chalk-marl.

Another considerable tract occupied by this rock extends in the valley of the Leine from Winzenburg across Sack and Wrisbergholzen to Gronau. It occurs also at Calenberg, at Hulfersberg near Sarstedt, at Kromsberg on the south-east of Hanover, at Gross Solchen near Peine, between Wöhlde and Wolfenbuttel, in the vale of Innersten, between Wartjenstedt and Liebenburg; quite on the north border of the Hartz mountains from Lutter at Barenberg, to Quedlinburg at Halberstadt; in Saxony near Weinböhla, Strehlen and Oberau; in the north

* Some of the identifications mentioned in this paper, of the German subdivisions of the chalk series, with those of England, appearing to be attended with doubt, it has been thought expedient to insert here both the German and English names: as of the flammen-mergel, plæner, and quader.—TRANS.

of Bohemia near Töplitz; in Silesia only at Oppeln*. It would be of no interest to describe more minutely the slight peculiarities which characterize these various localities.

Of minerals, the gray chalk contains calcareous spar and iron pyrites; the latter frequently in spherical, ovate or cylindrical masses, from 1 to 3 inches (1″—3″) in diameter. Sometimes, but very seldom, nodules, of the size of a fist or a foot, of a blackish hornstone, occur, as at Goslar. The sides of the fissures are for instance frequently coated with calcareous spar.

The following fossils appear to be characteristic of the (plæner) gray chalk-marl:—

Cœloptychium muricatum.
Micraster gibbus.
Terebratula pisum.
... Mantelliana.
... plicatilis.
... lævigata.
... ornata.
... pectita.
... semiglobosa.
Pecten Beaveri.
... depressus.
Inoceramus Brongniarti.
Inoceramus latus.
... striatus.
Cirrus depressus.
Turrilites costatus.
... tuberculatus.
Scaphites æqualis.
... costatus.
Ammonites Mantellii.
... Cottæ.
Hamites plicatilis.
... ellipticus.
Baculites obliquatus.

Ammonites are of frequent occurrence in the gray chalk. The most common is *A. varians*, which however already occurs also in the (upper) greensand; the *Turrilites* enumerated above, and likewise *Terebratula pectita*, appear to be confined to the older strata, while the two *Scaphites* first occur in the central layers. Both the *Belemnites* of the upper divisions of the chalk are no longer met with in the (plæner) gray chalk-marl, but we still find *B. minimus* in the lower beds. A very common fossil is the *Plicatula inflata*, which is readily distinguished, but it occurs also in the (upper) greensand; the most frequent *Echinodermata* are *Spatangus cor-testudinarium*, *Galerites albogalerus*, *Ananchytes ovata*, and *Cidaris claviger*, which belong in common to the (plæner) gray chalk-marl, and to the younger divisions of the chalk.

* From the absence of fossils we have not been able to identify with certainty, as belonging to this division, the gray schistose marl at Neuenwiese, between Goldberg and Löwenberg; it may possibly be Keuper.

IV. Upper Greensand:—Firestone, Merstham beds. [Der Grünsand.—*Glauconie crayeuse, craie chloritée.*]

This, according to Mantell, is in Sussex a sandy, argillaceous, grayish-green coloured deposit, consisting of marl and of granules of silicate of iron, which sometimes form loose, sometimes compact masses. It generally passes very gradually into the gray chalk (plæner); and varies in thickness from a few feet to 80. This formation is replaced in some districts by a bluish-gray compact chalk marl, which rarely alternates with green layers, and is called "malm."

At Folkstone this formation occurs as a soft gray sandy marl, which is traversed in all directions by stem-like cylindrical green-spotted bodies, and contains numerous granules of silicate of iron; its thickness here does not amount to more than 25 to 30 feet. At Godstone in Surrey, a deposit 4 inches in thickness of bluish-gray siliceous concretions (flints, chert) alternates with the green layers.

A similar description has been given of this formation in France.

In the North of Germany we meet very frequently with the flammen mergel (streaked marl), which appears to agree with the malm rock. The lower beds of the gray chalk-marl (plæner) sometimes gradually acquire a larger amount of clay, sand, iron and carbonaceous matter, and thus pass, or are suddenly changed, into a coarse earthy bluish-gray or yellowish-white marl, which is usually traversed by darker veins, streaks and spots, frequently exhibiting a thin slaty texture, and often alternating with harder and more siliceous seams, a few inches only in thickness. Not unfrequently, as at Simmenstedt, we find on this rock cylindrical, concentrically-wrinkled (concentrisch runzelige) concretions minutely spotted with green, about an inch in thickness, similar to those which occur at Folkstone; they frequently traverse the layers perpendicularly. This formation occurs thus beneath the plæner at almost all the places where we have pointed out the latter. Its thickness is frequently considerable, and sometimes, as for instance at Wrisbergholzen close to Alfeld, amounts even to 400 feet, though in general much less.

As regards the organic contents, *Avicula gryphæoides* (Sow. Geol. Trans. 2nd Series, iv. plate xi. fig. 3) appears to be especially characteristic; with this occur *Pecten laminosus, Belemnites*

minimus, Ammonites varians, A. Coupei, A. curvatus. It is perhaps likewise characteristic that *Inoceramus Brongniarti* and *I. Cuvieri* are not met with in this formation.

Of the localities where it is very distinctly exposed I will mention the high road just above Wrisbergholzen, the Ringelberg at Salzgitter, the quarry near the high road to the south of Simmenstedt close to Brunswick, the sand-pit at Goslar, and the quarries at Langelsheim.

The true *greensands* are more rare. We meet with them first of all in the south of Westphalia, on the southern limit of the chalk range, overlying the (flözleeren) sandstone.

Close to Werl, on the east, this formation is exposed in several quarries; that of Brunks affords the following section :—

	Feet.
1. Soil	2
2. Loam	5
3. Compact bluish-gray chalk-marl, frequently separated into spheroidal masses, alternating with very friable, more sandy marl, and inclosing *Inoceramus mytiloides*:—(Plæner)	4
4. Grayish chalk-marl, much rifted, tabular, tolerably compact, in layers 3 inches in thickness, and containing *Inoceramus Cuvieri, Ananchytes ovatus* and *Scyphia radiata*:—(Plæner, used for burning into lime)	7
5. Gray, sandy, compact, stratified marls, which contain numerous small granules of silicate of iron; the seams, from 4 to 6 inches in thickness, contain *Ammonites varians, Terebratula biplicata, Inoceramus striatus, Pecten laminosus,* &c.:—used for building	6
6. A more marly and softer stone, with very little silicate of iron.	

The last two layers belong to the greensand, and they also occur close to Bausenhagen, on the southern declivity of the Hartz.

The Greensand is well exposed in a fine quarry a few hours (stunden) to the south of Werl, on the northern side of the valley of the Waterlappe. Beneath a covering of soil, 2 feet in thickness, are 10 feet of greensand, reposing with a slight northern inclination on the (flözleeren) sandstone of the coal formation, which rises from the south at an inclination of 70°. The green-

sand here forms seams from 1 to 2 feet thick at the upper part, and from 3 to 4 feet below. The upper beds consist of a very argillaceous yellowish-gray compact calcareous marl, with little silicate of iron; the lower layers gradually lose the lime, and acquire much sand and much silicate of iron, become of a dark green colour, crumble very much by exposure to the air, and sometimes contain chalcedony and concretions of flint; the oldest strata contain large boulders of flint, clay-slate and sandstone. The following fossils occur here:—

Terebratula biplicata.	Ammonites falcatus.
Ostrea serrata.	Nautilus simplex.
Holaster subglobosus.	... elegans.
Ammonites varians.	Inoceramus concentricus (?).

To the east of the place last mentioned, the greensand may be traced under similar conditions, on the northern side of the Hard to Erwitte; and on the southern side, across Neheim, Mulheim and Belecke, to Rüthen.

The greensand exposed by the railroad cutting at Oberau, near Dresden, is perfectly similar to that above described. Here a dark grayish-green sandy marl, in which are diffused numerous blackish-green granules of silicate of iron, lies beneath the gray chalk: these granules increase in quantity in the lower portions; and the stone gradually contains a large number of fragments of decomposed granite or gneiss, so as to become a true conglomerate. It rests immediately upon the mass of gneiss, or is separated from it only by a small layer of a grayish-white decomposed sandstone, which abounds in organic remains. This formation contains among other fossils,—*Terebratula ovoides* (?), *T. biplicata, Ostrea carinata, Pecten notabilis,* and *Sphærulites*; and it has been observed under perfectly similar conditions in Elbstollen (?).

The glauconitic stone which occurs on the Waterlappe and at Oberau likewise perfectly resembles the firestone from Handfast Point in Dorsetshire, England; as we have convinced ourselves by the examination of specimens.

According to the above descriptions, we are still left in doubt, whether the banded marl (flammen-mergel), or the greensand is the older formation of the two: but the neighbourhood of Goslar settles this point most satisfactorily, the layers between the chalk-marl and the lower greensand being entirely exposed to view both

in the neighbouring sand-pit and close to Langelsheim. We find here beneath the gray chalk-marl (plæner)—

	Feet.
1. Streaked marl (flammen-mergel), with *Avicula gryphæoides* and *Pecten laminosus*; becoming in the lowest part gradually more sandy, and containing siliceous concretions	100
2. Clay-marl, traversed by numerous bands of hydrated oxide of iron	3
3. Soft (milde), sandy green marl, with numerous small granules of blackish-green silicate of iron, containing gray nodules of limestone from 1 to 2 inches in diameter	2

This last stone perfectly corresponds to that of the Waterlappe and of Oberau, and is therefore older than the greensand.

This formation also occurs, in a very peculiar form, to the right of the entrance into the vale of Plauen, near Dresden; where it forms a bed of conglomerate from 1 to 2 feet in thickness, which rests upon sienite, and probably fills the fissures in that rock. It is a siliceous chalky mass, bearing some resemblance to hornstone, and includes rounded fragments of sienite; and it contains *Sphærulites ellipticus, Pecten æquicostatus, Terebratula ovoides*, &c.?

Avicula gryphæoides appears to belong only to the (flammen-mergel) streaked marls; in which, on the other hand, we have never found *Terebratula biplicata*, which occurs in all the older chalk formations.

These streaked marls (flammen-mergel) and the greensand might be separated from one another with as much reason as these two from the chalk-marl, and as the upper from the lower chalk; but we shall leave this innovation to others.

V. The Gault:—Gault, Folkstone marl, blue chalk-marl. [Der Galt.]

In England the name *Golt*, or *Gault*, is applied to a deposit, from 4 to 150 feet in thickness, consisting of a compact clay, from a light gray to a dark blue colour; which contains about 30 per cent. of carbonate of lime, and frequently includes numerous laminæ of mica, and small crystals of gypsum. The upper portion is generally somewhat sandy, and mixed with granules of green silicate of iron. Spherical or cylindrical masses of iron

pyrites frequently occur in it; sometimes also in the interior (brown coloured nodules), which contain 57 per cent. phosphate and much carbonate of lime, and have been supposed to be coprolites. The fossils appear to belong principally to the lower division, the more pure and plastic clay; in which the following are especially frequent:—

Ammonites splendens.	Hamites attenuatus.
... lautus.	... tenuis.
... biplicatus.	... rotundus.
... auritus.	... compressus.
... tuberculatus.	... maximus.
... denarius.	Belemnites attenuatus.
... subcristatus.	... Listeri.
Inoceramus sulcatus.	Dentalium striatum.
... concentricus.	... ellipticum.
Rostellaria carinata.	... decussatum.

This formation has been hitherto unknown in Germany, and we have only been able to discover some slight traces of it at Goslar and Sarstedt. In a sand-pit near the first-mentioned town, and at the neighbouring village of Langelsheim, the greensand is succeeded by

	Feet.	Inch.
1. Bluish-black schistose clay	0	6
2. Yellowish-gray schistose argillaceous marl . .	1	6
3. A more compact yellowish-gray and reddish marl	0	2
4. Yellowish soft clay	1	0
5. Friable yellowish coarse-grained sandstone . .	2	0
6. Lower greensand	36	0

There appear to be no fossils here in these argillaceous strata; their mineralogical character and their stratigraphical relations might however admit of their being regarded as gault.

Close to Sarstedt, at the southern foot of Hulfersberg, a yellowish-gray, soft schistose marl was exposed to view during the last year, by the construction of a road beneath the banded marl. It is about 20 feet thick, alternates with some harder layers of marl, and contains in some places calcareous concretions of sever l inches in diameter; we found the specimen of *Hamites compressus*, represented in our Plate, in this argillaceous deposit, which we therefore consider as gault.

Frederick Hoffmann has referred some deposits of the neighbourhood of Halberstadt to the gault; but I do not know what he can have taken for it: I have not seen there even the flammenmergel.

Fitton maintains his having observed the gault at Aix la Chapelle and at Liege*; we are however inclined to doubt the correctness of his observation, especially as neither chalk marl nor lower greensand are met with at those localities; only the upper members of the chalk occur there.

If the entire chalk formation were to be divided only into two sections, we should terminate the lower with the gault; since it contains a most peculiar creation, and very few fossils only which belong to the more recent deposits of the chalk-series.

VI. Lower Greensand:—Shanklin sand. [Der Quader:—*Glauconie Sableuse, gres Vert.*]

The entire formation consists in England of green, gray, red, yellow and white sand and sandstones; with subordinate layers of hornstone, limestone, and Fuller's earth.

In Kent, and part of Surrey and Sussex, three subdivisions of it may be distinguished, which are—

1. The upper; consisting of sand with concretions of limestone, iron and hornstone; which latter are there called "chert," and possess a grayish-yellow or greenish colour, conchoidal fracture, and a glimmering lustre (Schimmernden Glanz).
2. The central; consisting of argillaceous and ferruginous greensand.
3. The lower; consisting of sandstones, which are frequently coloured green by silicate of iron, and contain a larger amount of lime; they are called "Kentish rag."

The total thickness of the lower greensand has been estimated in England at 400 feet†.

* On this point M. Römer's information appears to have been inaccurate; the author here referred to having stated expressly that the gault is wanting at the places specified, and mentioned its absence as one of the principal circumstances distinguishing the subcretaceous series there from that of England. —See Geol. Soc. Proceedings, 1829, vol. i. pp. 163, 164.—Trans.

† During the last year it has been ascertained that the lower greensand, near Hythe in Kent, is about 406 feet in thickness; but that near Atherfield, in the Isle of Wight, not much less than 800 feet.—Trans.

In Northern Germany the Quader occurs always as a fine-grained sandstone, in numerous localities associated with the upper members of the chalk, but in very different stages of development.

Thus it passes close to Goslar, from Hartzbourg to Lutter, along the border of the Hartz, as an unstratified slightly fissured layer, about 36 feet in thickness, of a soft sandstone, varying in colour from white to brown, and containing no mica. It is sometimes traversed by hydrated oxide of iron, and sometimes it encloses chalcedony. At the Clus it forms a single perpendicular rock, with rugged sides.

It occurs of somewhat greater thickness on the north of Quedlinburg; but there, as also at Goslar, without fossils. It is in the former case thinly stratified, yellowish-brown, soft, somewhat coarse-grained, sometimes resembling quartz conglomerate, and is traversed by numerous ferruginous bands, and forms inconsiderable hills.

At Ottberg near Hildesheim, the great sandstone formation of the Heiligenberg rests upon the Hils-clay; it consists of seams from 6 inches to 2 feet in thickness, of a yellowish or gray, tolerably compact sandstone; which is streaked, and spotted brownish-red by oxide of iron. Hitherto no fossils have been found at this place, but nevertheless we regard the formation as belonging to the quader (lower greensand).

We find the Quader (lower greensand) more developed in the "Hils-mulde" (the *trough* of Hils), between Alfeld and Eschershausen. It has there a thickness of about 600 feet, forms the so-called Blossezelle and the Hilsberg, and consists of gray or white, sometimes firm, sometimes soft, pure, or marly sandstones, which enclose five seams of ironstone, some of which are worked for commercial purposes, and frequently contains secretions of chalcedony with masses of mountain pitch. The only fossils obtained from it are fragments of wood, with *Teredines* (Bohrwurmern), and indistinct *Pectens* and *Ammonites*.

Towards the west we next meet with this formation, in the Teutoburger Wald, and can trace it over Bielefeld to Iburg; at Horn it forms perpendicular rocks about 100 feet high. Near the Hulse at Rothenfelde, the more recent strata consist of a siliceous conglomerate with a ferruginous matrix; these are succeeded by white, friable, fine-grained sandstones, but which gradually become more charged with iron, being at first traversed by

numerous yellow undulating lines, and finally of a perfectly ochreous colour. Fossils are frequent in the large stone quarries on the northern declivity of the mountain, and among them occur—

Hamites gigas.	Thracia Phillipsii.
Ammonites Decheni.	... elongata.
Mya elongata.	

The most westerly occurrence of the "quader" is on the north of Recklinghausen in Westphalia. It here forms the Haard; and at Haltern the Annaberg, and the Hohemark. In the whole of this district it occurs sometimes as a whitish, but generally brownish or reddish, perfectly loose sand, sometimes 200 feet in thickness, which encloses numerous nodules of brown ironstone and quartz, from the size of a fist to that of a foot, and frequently hollow in the interior; and it alternates with nearly horizontal layers, from 2 to 3 feet in thickness, of a compact sandstone very much fissured, frequently passing into a quartz rock. Fossils are not rare in this peculiar deposit, especially *Pecten muricatus*, and *P. quinquecostatus*, *Exogyra*, *Chama costata*, *Mytilus eduliformis*, and *Inoceramus mytilöides* var. Among these there are no characteristic species; and it is therefore still possible that the whole of the deposit may be of a more recent age; it might perhaps likewise be considered as an equivalent of the upper white chalk.

In Saxony we find the lower greensand in the immediate neighbourhood of Dresden, on the left bank of the Elbe at Costebaude, Bannewitz, Welschhufe, Rippchen and Golberoda; but it is here difficult to determine the upper limit of the formation. At Bannewitz, for instance, the following succession of strata appears in the Burgck stone quarries:—

	Feet.
1. Loose matter, or rubbish	4
2. Yellowish sand marl	1
3. White, soft, fine-grained, much-divided sand . . .	4
4. White, almost loose sand, with innumerable minute spiral *Serpulæ*, and *Serpula septemsulcata* . . .	0½
5. Argillaceous loose sand	4
6. Two seams, each 10 feet in thickness, of a light compact sandstone, with *Exogyra columba*, *Cardium Neptuni*, *Pholadomya albina*, *Pecten æquicostatus*, &c.	20

The lower beds (6) we consider to be lower greensand; but we doubt whether the upper ones likewise belong to that division, or should be referred to the upper greensand and streaked chalk-marls (flammen-mergel). We have similar doubts with respect to the succession of the deposits between Rippchen and Gobbeln; where the upper, marly, micaceous, soft argillaceous stratified sandstones are separated, by a somewhat sandy bed of clay, of a light gray colour and about 3 feet in thickness, from the lower lighter-coloured and less stratified sandstones, which are spotted with iron.

The so-called '*shell-rocks*' at Coschutz, in the vale of Plauen exhibit a very remarkable outcrop of this deposit; they form five isolated blocks, a few feet in height, projecting in a straight line on the declivity of the mountain, and consist of numerous shells cemented together by a soft yellowish sandstone. Among these shells occur *Nerinæa Borsoni, Exogyra columba, Cardium Hilanum, Turritella granulata*; which will probably justify the age here assigned to this deposit.

The masses of sandstone which occur on the east of Tharandt, at Opitz, and to the west at Grullenbourg and Nieder Schöna, appear likewise to belong to the lower greensand (quader). The fossil plants for which these rocks are remarkable, occur at the last-mentioned place: the lower strata of the sandstone, which in no respect differs from those above them, alternate several times with layers from 3″ to 3′* in thickness, of a dark gray micaceous schistose clay; and in these are enclosed well-preserved leaves of ferns and dicotyledons, among which, apparently, is also a *Credneria*. The ferns are distinct from those of the Weald-clay; and the *Credneria* and other dicotyledons might almost induce us to consider the whole sandstone formation of that district as of the same age with that of Blankenburg.

Similar relations of the sandstone rocks as at Nieder Schöna, are said to have been exposed to view to the east of Dresden, at Quohren.

The greatest horizontal extent of the lower greensand (quader) occurs in the so-called "Saxon Switzerland," and in the north-easterly portion of Bohemia. It is there indistinctly stratified, often much rifted and fine or coarse-grained, white or yellowish

* The precise meaning of the marks attached to these numbers is unknown to the Translator.

sandstone, which in general contains little cementing matter, and encloses principally the following fossils:—

Pecten æquicostatus.	Exogyra columba.
Pinna decussata.	Inoceramus concentricus.
.... pyramidalis.	

The beautiful rocky country formed by this deposit and the upper-chalk-sandstone are generally known, and are probably unique of their kind.

In Silesia the lower greensand is distributed chiefly between Goldberg, Löwenberg and Bunslau. At Seiphenau, in the neighbourhood of the first locality, it forms rocks 80 feet in height, is exposed to view in several quarries, and consists of a few very thick seams of sandstone, separated by thin slaty layers. The stone is light gray, coarse-grained, has very little siliceous matrix, and contains very few fossils. The quader at Langenberg, near Pilgramsdorf, is similar in appearance; but it is best exposed to view in the Moissen quarries close to Löwenberg. There we have above 8 feet of stratified sandstones, beneath which are 40 feet of lower greensand, in three or four seams, not much divided; the upper beds are fine-grained, the lower resemble conglomerate; those of the middle contain in a thin layer numerous but generally indistinct fossils; especially *Pecten asper* and *P. æquicostatus.*

Between Löwenberg and Bunslau, north-east of Wenig Ragwitz, a seam of coal is explored which is from 12″ to 18″ in thickness; resting upon which occur, beginning with the lowest,—

	Feet.
1. Loam	1
2. Yellowish fine-grained sandstone . .	8
3. Yellowish fat fetter clay	3
4. Yellowish fine-grained sandstone . .	12

Similar beds of sandstone and clay occur beneath the coal, none of which appear to contain fossils; it is therefore impossible to decide with certainty whether this formation belongs to the quader or to the Hastings sandstone; the first however appears to us the most probable.

At Bunslau the lower greensand consists of seams of sandstone from 6″ to 1′ in thickness, which alternate with whitish somewhat sandy beds of clay of equal thickness; the celebrated Bunslau earthenware are made of this clay. We have not observed any fossils in it.

The formations which we have in the preceding pages referred to the lower greensand, are true sandstones; in which, exclusively, the following fossils appear to occur:—

Exogyra columba.	Inoceramus concentricus.
Pecten æquicostatus (var. major).	Cardium Hillanum.
Pinna quadrangularis.	... Neptuni.
... decussata.	Nerinea Borsoni.
... depressa.	

If we compare this list with the large number of fossils which have been described in England from the lower greensand, the latter will appear to be remarkably poor with us; but we shall find that the two following formations completely counterbalance this disproportion.

2. *Hils-conglomerate.* [Hils-conglomerate.]

This formation generally presents itself as a mass of granules of quartz and silicate of iron, which are cemented by a yellowish or gray, ferriferous calcareous marl.

The most westerly occurrence is in the district of the Ruhr, at Essen. Here the old coal formation predominates; but this in most places supports a horizontal layer, about 10 feet in thickness, of the conglomerate, which at the Hagenbecker Zeche appears as a greenish, small-grained, tolerably compact sandstone; but at other points as a yellowish-gray, highly ferruginous loose sand, with numerous grains of silicate of iron. On the western side of the town this formation,—which hitherto has been referred to the upper greensand, to which indeed it is very similar in mineralogical respect,—is covered by the gray chalk (plæner).

The Hils-conglomerate is found to contain still more iron at Steinlahte, close to Salzgitter in the valley of the Innerste; in the lower part are here yellow and blue slaty loams,—followed, in ascending order, by a yellow tolerably compact sandstone 25 feet thick,—which is succeeded by pure oolitic ironstone 7 feet in thickness,—separated by a thin stratum of a compact ironstone, from a sandy oolitic ironstone 5 feet in thickness; this last supports a very considerable mass of red, yellow and gray slaty loams, and these are succeeded by the streaked marl and gray chalk (flammen-mergel and plæner). The thickness of the deposit increases, in other points of the same range of hills, to 160 feet.

A third occurrence of the conglomerate is at Vahlberg on the

Asse, and Berklingen near Wolfenbuttel; where conglomerate rests upon the middle lias. It is tolerably compact, yellowish brown, small-grained, with a large proportion of a calcareous cement and numerous fragments of shells. In the stone quarry above the windmill at the first-mentioned place, six seams of this rock, 3 feet in thickness, were apparent, which were separated by thin layers of a softer marl.

The Hils-conglomerate occurs, with perfectly similar characters, only more stratified, on a hill to the north of Schandelahe near Brunswick; and without doubt also at Schöppenstedt on the Rothenberg.

There has also been recently exposed at Osterwalde by the "new light" shaft No. 1, above the Weald-clay, a ferruginous gray mass of sandstone 18 fathoms in thickness, which is sometimes fine-grained, sometimes in the state of a conglomerate, and which has been proved to belong either to the Hils-clay or the Hils-conglomerate by the presence of

Avicula macroptera.
Exogyra sinuata.
Modiola rugosa.
Terebratula varians, var.
Thracia Phillipsii.
Turbo clathratus.
Belemnites subquadratus.
Ammonites Nutfieldiensis.
Glyphea ornata.

This same deposit likewise occurs in the neighbouring Steinbach. It is succeeded, according to a communication of the mining officer M. Hartleben, by a sand, which above is fine-grained, below coarse-grained (1° 6′) (1 ft. 6 in.?); then slate-clay (1° 6′); blue marl (1°); limestone, called 'blue stone' (4′); then clay-slate (2°), with *Cyrena media*, Sow.,—therefore clearly belonging to the Weald-clay.

The number of fossils with which we have become acquainted from the Hils-conglomerate is already very considerable and will certainly still be augmented; the following species appear to belong exclusively to it, in Germany, where they are found at various places:—

Scyphia furcata.
... tetragona.
... foraminosa.
Manon peziza.
Chrysaora pustulosa.
Palmipora polymorpha.
Cidarites vesiculosa.
Cyphosoma rugosum.
Galerites subuculus.
Crania hexagona.
Terebratula latissima.
... nuciformis.

Terebratula depressa.	*Spondylus striatus.
Ostrea macroptera.	Thetis Sowerbii.
Pecten atavus.	Serpula angulosa.

There also occurs in it, at Essen, a small *Balanus*.

3. *Hils-clay*:—Speeton clay. [Der Hils-thon.]

At the northern foot of the Deister, at Bredenbeck and Wennigsen, is situated, immediately upon Weald-clay, another grayish-blue argillaceous mass, about 60 feet thick, which contains numerous roundish nodules of a grayish-brown compact limestone, knobs of iron pyrites and small crystals of gypsum. This is the Hils-clay.

It occurs with the same character on the northern foot of the Galgenberg at Hildesheim; especially at the villages Achtum and Wendhausen, and is continued at Farinsen and Laffarde.

A third and better known locality is in the *Hils-mulde** (the "trough of Hils"), close to Alfeld. This argillaceous mass is here met with nearly everywhere beneath the quader; and is, especially at Elligserbrink, where formerly a seam of ironstone, 4 inches in thickness, was worked, a well-known and rich locality for fossils. It is likewise exposed on the southern declivity of the Hils, by several water-courses. In many parts of the Hils-mulde, large unstratified masses of a compact spotted gypsum occur in it, which at Weenzen frequently contain an excretion (ausscheidung) of pure sulphur, with sometimes earthy, sometimes slaggy, mountain-pitch. The mineral springs at Lauenstein likewise appear to originate in this clay.

Judging from some of its fossils, the Hils-clay would appear to occur at Rehburg, and in the neighbourhood of Salzgitter and Liebenburg; where however we have not seen it in person. It also appears under perfectly similar relations, under the form of a schistose, sometimes white-spotted clay-marl, called Töck, in the island of Heligoland, and there affords numerous fossils which are mostly converted into iron pyrites.

In the sand-pit at Goslar is seen, beneath the quader (lower greensand), a mass which at the upper part consists of about 2

* The names of this deposit, and of the *Hils*-conglomerate, are taken from the place here mentioned, of the vicinity of which a map will be found in Hoffmann's *Geognostische Charte vom Nordwestlichen Deutschland*, in 21 plates:—Berlin, 1829. Some other sheets of that valuable map will also be found useful in perusing the present translation.—TRANS.

feet of yellowish oolitic iron ore, and beneath of a dark gray clay about the same thickness. Neither of these parts contains any fossils, but from their stratifical relations they may probably belong to the Hils-clay.

Some former geologists referred the argillaceous deposit, which was first observed at Elligserbrink, to the Oxford clay, others to the Kimmeridge clay; and I myself have since considered it as the youngest member of the Jura: but subsequently I became convinced, from observations at the foot of the Deister, that it was superior to the Weald clay; and, at a later period still, I recognised in it the Speeton clay of English geologists. That the Speeton clay is in England considered, without sufficient reason, as an equivalent of the gault, is evident from the relations of stratification in the Hils-mulde, where the gray chalk distinctly overlies the argillaceous mass; and moreover from the distinctness of its fossils from those of the gault.

The following fossils appear to be restricted to the Hils-clay in Germany:—

Modiola pulcherrima.
Isocardia angulata.
Panopæa plicata.
Fistulana constricta.
Belemnites pistillum.
Ammonites rotula.
... asper.
Hamites Beanii.
Hamites obliquecostatus.
... fissicostatus.
... raricostatus.
... capricornu.
... sexnodosus.
... decurrens.
Serpula Phillipsii.

Numerous fossils of the Speeton clay are found also in the Hils-conglomerate; for instance—

Heteropora ramosa.
Pentacrinites annulatus.
Crania irregularis.
Terebratula multiformis.
... oblonga.
... longa.
Exogyra sinuata.
... haliotoidea.
Pecten cinctus.
Avicula macroptera.
Modiola rugosa.
Belemnites subquadratus.
Ammonites noricus.
Serpula antiquata.
Glyphea ornata.

Other species ascend in Germany from the Hils-clay into the gray chalk; for instance—

Pecten asper.
Thracia Phillipsii.
Mya elongata.
Hamites gigas.
Catopygus carinatus.

But the number of those species which occur also in the English quader (lower greensand), and were first described from English localities, is far more considerable; for instance—

Terebratula Gibbsiana.	Exogyra haliotoidea.
... latissima.	Pecten orbicularis.
... nuciformis.	... asper.
... depressa.	Spondylus striatus.
... oblonga.	Modiola lineata.
... biplicata.	Venus parva.
Ostrea macroptera.	Thetis minor.
Exogyra sinuata.	Panopæa plicata.
... conica.	Hamites gigas.
... plicatula.	Ammonites Nutfieldiensis.
... undata.	Serpula antiquata.
... harpa.	

From these comparative lists, it is evident that the Hils deposits are very closely related to the quader (lower greensand); and it now therefore only remains to be ascertained in what relation they stand to it, and to each other.

The stratigraphical relations, and especially the discovery of *Ammonites asper*, indicate a great resemblance of the Hils-clay to the Terrain Néocomien, on which subject we have given our opinion in a former publication. But it was not until after the appearance of that work that we learned from the *Bulletins de la Société Géologique de France*, that the Néocomian has been detected in that country likewise in several localities, and that its relations there are perfectly similar to those above described. If we compare with these relations the observations of Dubois de Montpereux and De Verneuil in the Crimea, the occurrence of Néocomian in those countries likewise is placed beyond a doubt, and the following table illustrates the agreement of these various deposits:—

THE LOWER CHALK FORMATION.

At Neufchatel in Switzerland.	*At Auxerre in the Department of the Yonne.*	*In the Department of the Aube.*	*At Wassy.*	*In the Crimea.*	*In North Germany.*
Lower greensand (quader).	Bed of hydrated oxide of iron; ferruginous sandstone; yellowish micaceous sand; large seams with *Gryphæa sinuata.*	Lower greensand (quader). Clay with *Exogyra sinuata.*	Greensand. Yellowish sand.	Lower greensand (quader) with *Pecten orbicularis.* *P. quinquecostatus.* *P. laminosus.* *Exogyra decussata.* *Ostrea diluviana.*	Lower greensand (quader).
	Red and gray spotted clays: Lumachelle with *Exogyra harpa,* *Pecten quinquecostatus,* and a small *Corbula.*	White, red, yellow or green-spotted clays; which contain oolitic iron, and *Exogyra harpa.* *Cardium Hillanum.* *Pinna gracilis.* *Astarte similis.*	Gray, blue or yellowish-green clay; which alternates with ferruginous sand and sand-stone, and contains *Plicatula radiola.* *Ammonites splendens.* *A. complanatus.*		Hils-conglomerate.
	Gray schistose clays, alternating with ferriferous oolitic marls, and containing numerous large oysters.	Gray and grayish-blue clays, with Lumachella and *Ostrea.* *Exogyra harpa.* *Lima elegans.* *Cytherea Vendoperana.* *Corbula punctum.* *Cardium impressum.*	Gray clay alternating with marly Lumachella; and containing numerous oysters and crystals of gypsum.		Hils-clay.
Yellow limestone. Blue marl with *Ammonites asper.* *Spatangus retusus.* *Serpula heliciformis.* *Terebratula depressa* (?) *Gryphæa Couloni.* Yellow limestone, with ferruginous sandstone (Eisen-sandstein).	Compact limestone with granules of silicate of iron. *Spatangus retusus.* *Trigonia alæformis.* *Pecten quinquecostatus.* *Pteroceras Pelagi.*	Light coloured limestones, passing below into beds of white and yellow sand. *Pholadomya Langii.* *Trigonia alæformis.* *Pecten striato-costatus.* *Exogyra sinuata.* *Pteroceras Oceani.* *Nautilus elegans.* *Ammonites asper.* *Spatangus retusus.* *Nucleolites Olfersii.*	Yellow argillaceous marls, with crystals of gypsum.—Yellowish white limestone, with *Spatangus retusus*; passing below into blue calcareous marl.	Whitish or bluish marl, with *Ammonites asper* and *Ceriopora micropora.* Yellow limestone and sand with *Exogyra Couloni.* *Lima.* *Terebratula nicinalis* (?). *T. biplicata, dyphia, flabellulata* (?). *Ammonites hircinus* (?), *dubius* (?). *A. Brongniarti* (?), *perarmatus* (?). *Hamites intermedius.* *H. plicatilis.* *Ceriopora dichotoma, micropora.* *Scyphia furcata, Œynhausii.* *Astrea tubulosa.* *Turbinolia.* *Lithodendron,* &c.	

In the preceding synoptical table we meet, beneath the quader, first, variegated clays, ferruginous sandstones and Lumachellas; then gray argillaceous masses with subordinate marly Lumachella; and, finally, light-coloured limestones and bluish marls,—the formation of the so-called "*Spatangus*-limestone."

This last-mentioned deposit appears to be entirely wanting in the North of Germany, as well as the fossil species, *Pteroceras Pelagi* and *Spatangus retusus*; at least we are not acquainted with any calcareous or marly deposit in Germany which can be referred to it. Our Hils-clay and Hils-conglomerate must therefore belong to the middle sections of the above table. We have nowhere been able to detect a superposition of the one deposit over the other, but if we take into account the general character of the fossils, the Hils-clay appears to be the older formation. *Terebratula latissima, T. depressa, T. nuciformis, Pecten asper, P. quinquecostatus*, and *P. æquicostatus*, as well as *Ostrea macroptera*, true chalk forms, have not yet been found in it; on the other hand, the *Hamites* of Heligoland and Speeton certainly agree for the most part with those found in the Crimea. *Ammonites asper* likewise appears to belong to the older Neocomian, and several other Ammonites, e. g. *A. venustus, A. Phillipsii, A. rotula*, exhibit a greater affinity to those of the Jura than those of the Hils-conglomerate.

Under these circumstances we consider ourselves justified in considering our Hils-clay as equivalent to the gray schistose clays which in France overlie the *Spatangus*-limestone; and look upon the Hils-conglomerate as parallel to the Lumachellas, which are met with there above those gray clays and beneath the variegated clays of the chalk-marl. At Salzgitter the conglomerate is subjacent to an argillaceous mass, which is perhaps of the same age as the variegated clays.

It is difficult to prove the correctness of these parallels, till the fossils occurring in the Neocomian in France have been described: it is to be hoped that this will very soon be done.

Most of the argillaceous masses in the south of England which have been described by Fitton, with the inferior portion of the lower greensand, as "Fuller's-earth," will undoubtedly prove to be equivalents with the Hils-clay. It is scarcely possible that the deposit should be absent there, since it has been discovered in Yorkshire, in Heligoland and in France.

Some French geologists are of the opinion that the Weald-clay

formation originated at the time when the ocean deposited the Neocomian; since however the Hils-clay on the Deister, and the Hils-conglomerate at Osterwald, are most decidedly superior to the Weald-clay, that contemporaneity of origin is conceivable only with respect to the true *Spatangus*-limestone; and this appears to be entirely absent in England and in North Germany, where on the other hand the Weald-clay formation is pre-eminently developed. It will perhaps be possible to determine the true relation of the Neocomian to the Weald-clay in the Alps.

General Stratigraphical Relations of the several Groups above mentioned.

Having considered the separate portions of the north German chalk formation, and endeavoured to establish their palæontological characters, we have still to give an idea in a few lines of their general stratigraphical relations.

The first point here deserving of observation is, that the chalk formation is found only on the southern borders of and within the low region in North Germany, which is covered with sand, and cannot be traced southwards even so far as the oolitic formation. This is evident, for instance, in the valley of the Leine, where the lias reaches to Gœttingen, but the chalk only to the neighbourhood of Vincentburg near Alfeld. If, moreover, we bear in mind that no further trace of the chalk formation can be detected in the whole district between the Wirtemberg and the French Jura, it is evident that, after the deposition of the oolitic mountains, considerable upheavings must have added very much to the land, but have encroached upon the ocean at that period. That similar upheavings were likewise continued or repeated, during and after the deposition of the chalk formation, is self-evident, since its strata, when they are not perfectly horizontal, frequently exhibit a considerable inclination, and are even sometimes thrown backwards with a reversed dip. In the western portion of our district, at Aix-la-Chapelle, we find only the upper, at Vaëls, only the lower chalk marl; they rest almost horizontally upon the older coal formation, and do not appear to have been subjected to any upheaving subsequent to their deposition.

In Westphalia we find several separate ranges of hills belonging to the chalk formation; thus the plæner (gray chalk-marl) at Ahaus,—the upper chalk-marl at Dulmen,—the lower at Coes-

feld and Osterfeld,—the quader (lower greensand) at Haltern and Recklinghausen,—the Hils-conglomerate resting upon the older coal formation at Essen,—are all horizontally stratified and not upheaved; but the whole of the ancient bay is inclosed by the chalk. From Essen on the Ruhr, across Unna, Soest, Werl to Padeborn, we find gray chalk (plæner) resting upon the (upper) greensand, slightly inclined towards the low land and deposited on the (flözleeren) sandstone; these formations then continue northwards in the Teutoburg Wald, are there accompanied by the lower greensand, and with it rest upon the salt formation; they become likewise gradually more elevated, and then soon turning westwards, are separated at Bielefeld and Iburg from the salt beds by the Weald-clay, and are there completely turned back, probably by the gypsum of the salt formation, so that the lower greensand (quader) rests upon the banded marl (Flammenmergel) and the gray chalk (plæner).

To the west of the Weser we again meet with the lower chalk-marls at Lemförde and Haldem; north of Osnabruck they lie almost horizontally, and form a considerable hill.

Between the Weser and Leine we find, in the first place, on the northern declivity of the Deister, Hils-clay; it rests there, at Bredenbeck, immediately upon the Weald-clay, and has a slight northerly inclination; a mile further to the north it is overlaid, at Gehrden, by the upper chalk marl in tolerable thickness, forming a considerable hill, but apparently declining equally on all sides. At Osterwalde the Hils-conglomerate rests in a similar manner upon the Weald-clay; and here it is surmounted only by a mass of loam.

More to the north, and close to Hanover, the lower white chalk-marls are deposited on the northern declivity of the Lindenberg; they rest upon the upper division of the oolitic group, extend as far as Limmer, and are cut through and exposed to view by the Leine.

To the south of the places last mentioned we meet with the (plæner) gray chalk, (Flammen-mergel) streaked marl, (quader) lower greensand and Hils-clay,—all in what we have called Hilsmulde (the "trough of Hils"), between Alfeld and Eschershausen. They all rest upon the Portland and Purbeck limestones; perhaps also in some places upon Weald-clay, throughout a space four miles long, filling an oval trough of the oolitic formation, and inclining towards that (oolite) deposit under a small angle.

Still more considerable masses belonging to the chalk formation occur between the Leine and the Elbe. In the first place, close to the Leine, between Gronau and Vincentburg, the chalk-marl (plæner), banded marl (Flammen-mergel), and lower greensand (quader), form a considerable range of mountains,—the Siebenberge, the Sackwald, &c.; and the first two of these deposits, especially the plæner and Flammen-mergel, are here very strongly developed. The lower greensand appears to rest at this place immediately upon the Dogger (lias clay), and is but little raised.

At Sarstedt we observe, on the Hulfersberg, the same deposits, gray chalk (plæner), and banded marl (Flammen-mergel), inclining northwards; and some hundred paces to the south, apparently the gault also, with *Hamites compressus*. The same mountain range continues behind Algermissen to Solschen; the lower plæner (gray chalk), forms to the north of it the heights at Rethen, the upper gray chalk (Ober-plæner), the Kronsberg; the lower chalk marl occupies, without appearance of disturbance, the district between Ilten and Ahlten, between Oberg and Gadenstedt, that of Schwicheldt, Meerdorf and Dudenstedt, everywhere abounding in fossils.

Near Hildesheim the Hils-clay is deposited on the northern foot of the upper Jura, and strikes over Achtum, Wendhausen and Farmsen to Lafferde; the lower greensand rests upon it at Ottbergen,—and upon this the plæner (gray chalk), which may be traced across Nettlingen and Sehlde as far as Lengede.

A much more extensive chalk deposit commences at Waitjenstedt and Lutter, on the Barenberg; it appears along the entire northern border of the Hartz mountains, and terminates only beyond Blankenburg. The principal mass is formed upon (plæner) gray chalk-marl, which rests upon (Flammen-mergel) streaked marls, (upper) greensand, (quader) lower greensand, Hils-conglomerate, and Hils-clay; and, from Goslar to Blankenburg likewise supports considerable masses of the upper and (at Ilseburg) lower chalk marl. All the strata appear to be strongly elevated close to the border of the Hartz, or, as at Goslar, even to be thrown backwards; but at some distance they present a much smaller inclination. At Quedlinburg this chalk formation forms a double trough; one between Thale and Quedlinburg, the other between this latter place and Halberstadt. The lower greensand however constitutes there the oldest deposit, and appears at

Quedlinburg to rest immediately upon the lias. The upper chalk-marls are much raised on the Schlossberg, at Wernigerode; but appear, on the contrary, to have been little affected by the last upheaving on the Sudmerberg at Goslar.

This chalk formation extends in the valley of the Ocker, northwards, as far as Brunswick; and eastward probably lies immediately upon the Muschelkalk of the Elm. It rests however, at Wahlberg on the Asse; and at Schöppenstedt, upon the lias: an insulated portion of the Hils-conglomerate appears to have the same substratum at Schandelahe, north-east of Brunswick.

More to the east we again meet with the chalk formation only in the valley of the Elbe itself, close to Dresden. At Oberau the gray chalk (plæner) and the upper greensand (grünsand) have been very beautifully exposed by the construction of the railroad tunnel; and besides the plæner, arenaceous equivalents of the Flammen-mergel, and quader (banded marl and lower greensand), extend on the left bank of the Elbe, as far as Pirna; where the lower greensand (quader), with incumbent chalk sandstones and subordinate Flammen-mergel (streaked marls), apparently constitute the principal mass of the tract called "Saxon Switzerland." The enormous masses of sandstone have here an almost horizontal position, and hence are found to occupy a great expanse; on the eastern border only they are sometimes raised to a vertical position, or even reversed by the action of Plutonic rocks.

The masses of lower greensand (quader), on the northern border of the Riesengebirge, between Goldberg and the Queiss and the Neisse, appear likewise to have been little subjected to disturbance, and to rest (at least in all the places observed by myself) almost horizontally on the salt formation. Still further towards the east I myself have not examined the chalk deposit.

General Palæontological Character of the Chalk Formation.

We shall now briefly describe the general character of the remains of the animal and vegetable kingdoms imbedded in the chalk formation.

But few remains of the latter have on the whole descended to us, and these have been as yet only partially described: they consist of some Algæ and several Ferns, a few *Cycadeæ*; but

with some forms (*Credneria*) which we must undoubtedly refer to the Dicotyledons. The whole of these last-mentioned productions are probably restricted to the most recent chalk deposits, and are the oldest members hitherto discovered of the most highly developed and largest division of the vegetable kingdom; which renders them peculiarly interesting.

The animal kingdom is far more prolific in preserved forms; they are however only such as inhabit the ocean, and the entire chalk formation is therefore evidently and almost exclusively a marine deposit.

The *Sponges* (Seeschwämme), however, which are especially numerous in the Hils-conglomerate (lower greensand), and in the lower chalk, belong for the greater part to such genera as are met with in the oolitic series, and have moreover representatives at the present time. The *Scyphiæ* and *Siphoniæ* are predominant: but the *Cœloptychiæ*, which are restricted to the upper deposits of the chalk, are especially characteristic from their perfect development.

Of *Corals*, there occurs an almost innumerable host of minute *Bryozoa*, especially in the most recent chalk strata; and several genera (*Chrysaora*, *Heteropora*, *Thalamaropora*, &c.) appear to have there become extinct. The *Zoanthariæ* occur in general very sparingly, and even beyond the limits of our district. At Maestricht, for instance, where the greatest number of them have been found together, they do not appear to have formed large masses, as was the case during the deposition of the coral rag.

The *Radiata* are likewise very numerous, with many peculiar genera; the *Eugeniacrinites*, *Apiocrinites* and *Pentacrinites* here occur for the last time, and appear, especially the latter, not to differ very much from older species. *Marsupites* is entirely restricted to the upper chalk; *Glenotremites* to the Hils-conglomerate (lower greensand): *Galerites*, *Schizaster*, *Micraster* and *Ananchytes*, attain to their greatest profusion of species in the upper beds of that group; *Holaster* in the central beds; and *Galerites* there becomes extinct.

Among the *Brachiopodæ*, the so-called *Rudistæ* (*Sphærulites*) are most prominent, since they appear to have existed everywhere, from the period of the lower greensand to that of the upper chalk, and the present creation scarcely presents similar beings; but the climate of our latitude appears to have been less favourable to them, than that of the southern coasts of the

islands which were at that time formed by central Germany and France. At the same time, the *Craniæ*, which are most closely allied to them, exhibit their greatest development; and the *Terebratulæ* never again occur in like profusion. The plicated species of the latter genus became extinct in the upper chalk formation; and those found in the older chalk differ from those of the oolitic group in the folds on the back (*am* Buckel) partly dichotomising. The *Dichotomæ*, which in earlier deposits occur but sparingly, here become very numerous; and such forms as *Terebratula gracilis* and *T. pulchella* are quite as peculiar to the chalk as the species allied to the *T. carnea*; *T. biplicata* of the chalk it has hitherto been impossible to distinguish with certainty either from the Jurassic or from the living form. The *Thecideæ* are likewise here more developed than in other periods; but they are by no means equal to the *Terebratulæ* in the variety and abundance of their forms.

With respect to the *Conchiferæ*, the *Dimyaria* are proportionately more numerous than in older rocks, but still they are exceeded by the *Monomyaria*. Of *Oysters*, the older strata especially still contain species with longish shells, acutely dentated on the perpendicular margin, as they (first) occur in the Jura. The *Exogyræ* occur in very large forms, and then die out. Among the *Pectinites* the natural group of the *Neitheæ* is restricted to the chalk, but occurs in nearly all its beds. *Spondylus* and *Inoceramus* present a great abundance of forms; the latter is highly developed, especially in the gray chalk, and becomes extinct with the chalk formation. *Avicula* contains the newest longitudinally ribbed species. *Pectunculus* has already several large species, which call to mind those of the tertiary deposits. *Astartes* are very rare. The *Cardiæ* approach, by some species which are perpendicularly truncated in front, to several living forms. *Thetis* appears to be confined to the older chalk deposit. *Tellina*, *Donax*, *Teredo*, *Teredina* and *Fistulana* here exhibit, for the first time, decided representatives. *Goniomya* occurs for the last time in the upper chalk. *Pholadomya* is likewise poorer in species than in the Jura, and presents no peculiar forms.

Among the *Gasteropoda* (Schnecken), forms which call to mind *Auricula* are frequent. *Rostellaria* contains several large species. *Pyrula* and *Voluta* occur for the first time in the upper chalk. One species of *Nerinæa* still occurs in the lower greensand, and there terminates its brief existence. On the other hand, we find

in the upper chalk the first true *Turritellæ*, which, we at least, have not seen from any older deposit. Several large species of *Pleurotomaria* still occur; *Trochus* and *Turbo* have likewise numerous representatives. *Cerithium binodosum* is for the greater part more allied to the more recent species than to the older. *Delphinula* is probably wholly absent in the older deposits.

With respect to the *Cephalopods*—we have *Nautilus*, with few, but very widely distributed, species. The *Belemnites* of the lower greensand are neither furcated nor have a fissure inferiorly; the few belonging to the upper chalk have a fissure in front at the base, and with these this peculiar race, so prolific in species, dies out:—and with them the more beautiful *Ammonideæ* disappear. Of these the *Falciferæ* and *Amaltheæ* no longer occur in the chalk formation; and only the forms which resemble *A. Lamberti*, in the Hils-clay. The *Planulatæ* and *Dorsatæ* are still tolerably frequent in the older chalk deposits, and appear to become extinct in the gray chalk. The *Macrocephalæ*, *Ornatæ*, *Dentatæ* and *Armatæ* continue most frequent. The *Ammonites* of the chalk are, as their most talented friend (Von Buch) says, in general sickly*; many appear too weak to be able to combine the earlier convolutions: these are therefore left free, as in (*Hamites*); and are at last straight (*Baculites*). Similar causes have also produced the *Scaphites* and the *Turrilites*. *Ammonites bidorsatus*, *Baculites anceps*, *Hamites intermedius*, *Turrilites undulatus*, *Scaphites inflatus* and *binodosus*, appear to be the last of their respective races:—their latter days they passed amidst a legion of minute, chiefly microscopic, delicate, allied forms, among the *Rhizopods* (*Foraminifera*?). These last-mentioned forms we meet with for the first time in the Hils, the lowest clay of the lower greensand, in large quantity; and they are so frequent in the white chalk that this stratum consists perhaps altogether of a deposit of their shells; the majority of their tertiary genera likewise occur in the chalk formation; *Agathistegiæ*, however, appear to be wholly absent.

Annelidæ are numerous, but offer little remarkable.

Among the *Crustacea*,—*Cytherinæ* are not rare in the Hils-clay and the upper chalk; they are all very similar to the tertiary species. *Pollicipes* first occurs in the Hils-clay; *Balanus* in the Hils-conglomerate (lower greensand): the upper chalk deposit contains several species of the former genus, and at the same time

* "Wie ihr gestreichsten Freund sagt, 'meist krank.'" (Orig.)

also the oldest *Anatifa*. Of *Crabs*, the Jurassic genera *Glyphæa* and *Klytia* (?) continue in the chalk, and there become extinct: with them *Palæmon* (?) is associated, and, it would appear, the still living genus *Calianassa*.

If we now turn to the remains of the more highly developed animals, we find these not to be very numerous. As yet scarcely thirty species of *Fishes* have been discovered: but they belong to the four principal divisions; and, what is most remarkable is, that recent genera, for instance *Beryx*, should likewise occur amongst them; others appear in the older rocks. The *Saurians* are still more rare, the remains of three species only having been discovered; but no traces of *Birds* and *Mammalia* have been hitherto detected.

The creation of the chalk period approaches considerably to that of the present epoch, in the absence of older forms, and the reception of others which are more recent; but it still appears to be as much distinguished from the modern epoch as the older formations, no decided species of the chalk having hitherto been proved with certainty to exist in any other formation. That the climate of the chalk period was much warmer in our latitudes than at present, can scarcely be maintained from the fossils, since only the large *Saurians* and some *Cycadeæ* afford ground for the supposition.

Conclusion.

Having now become acquainted with the numerous and varied fossils of the chalk formation of the north of Germany, and with their assistance established the relative age of the strata in which they are imbedded, it will be apparent that this formation is here so rich, that but few other regions can show an equal variety.

The principal results of our geognostic researches, we trust, will be recognised as correct. The main points for subsequent investigation will be,—To ascertain Whether the mass of rock between Recklinghausen and Haltern belongs to the lower greensand or to the upper chalk marl?—Whether the gault does not occur in several other districts?—Whether the Hils-clay is really older than the Hils-conglomerate?—Further; Of what age are the more recent sandstones of the "Saxon-Switzerland," according to their fossils?—and, In what relation does the entire north European chalk formation stand to that of more southern districts, especially to the Nummulite and Hippurite limestones?

The following Table, prefixed by the Author to his first number as a "Notice," will be a useful summary of the foregoing pages, and may serve as an Index.

General View of the several Groups of the Chalk Formation.

I. UPPER CHALK. [*Die obere Kreide.*] With numerous small corals, and (?) without Ammonites. To this division belong, and are of *equal age*, the following:—

1. *Upper Chalk*:—White chalk with flints (of Rügen), p. 116.
2. *The Maestricht Limestone* beds, and those of Aix-la-Chapelle, p. 118.
3. *The Upper White Chalk Marl and Sandstone.*
   (Of Gehrden, Goslar, Halberstadt, Spiegelberg, Sudmerberg, Quedlinburg), p. 120.

II. LOWER CHALK. [*Die untere Kreide.*] Chalk without flints, with *Scyphia* and *Cœloptychia*, p. 125.

1. *Lower White Chalk.* [Untere weisse Kreide.] Chalk without flints.
   (Of Schwicheldt, Meerdorf, Teidessen (near Peine), Hanover, Luneburg, and Oppeln), p. 125.
2. *Lower White (Sandy) Chalk Marl.* [Der untere Kreidemergel.]
   (Of Ilseburg, Staplenburg, Lemförde, Coesfeld, Dülmen, Vaels, Oberau in Saxony), p. 125.

III. GRAY CHALK MARL. [*Die Plæner.*] Chalk marl, with *Inoceramus Brongniarti*; without *Belemnites mucronatus.*
   (Southern Wesphalia, Teutoburger Wald, Laërberg, Sarstedt, Calenberg, Alfeld, Grünenplan, Harz, Wolfenbüttel, Dresden, Oppeln, and Töplitz), p. 127.

IV. UPPER GREENSAND. [Der Grünsand.]

1. *Flammen-mergel.* [Streaked marl.] With *Avicula gryphæoides*; almost universally accompanied by the plæner (gray chalk marl), p. 130.
2. *Upper Greensand.* [Grünsand, glauconie crayeuse.]
   (Southern Westphalia, Oberau and Vale of Plauen near Dresden in Saxony, Langelsheim near Goslar), p. 131.

V. GAULT. [Der Galt.]
   Ottbergen and Sarstedt near Hildesheim, Halle in Westphalia), p. 133.

VI. LOWER GREENSAND. [Quader.]

1. *Lower Greensand.* [Quader.]
   (Glatz, Pirna, Harz?, Heimberg, Hilsmulde, Teutoburger Wald, Aachener Wald?, the Haard in Westphalia), p. 135.
2. *Hils-conglomerate.* [Hils-conglomerat.]
   (Schandelahe, Vahlberg on the Asse, Salzgitter, Essen on the Ruhr), p. 140.
3. *Hils-clay*:—Speeton clay. [Hils-thon.]
   (Hilsmulde, Bredenbeck, the Deister, Rehburg, Hildesheim), p. 142.

Article VI.

Memoir on Daltonism [*or Colour Blindness*]. *By* M. Elie Wartmann, *Professor of Natural Philosophy in the Academy of Lausanne, &c.*

[Read at the Société de Physique et d'Histoire Naturelle de Genève, April 16, 1840*.]

I.

Introduction.

MANY persons, whose eyes are sound and capable of performing their most delicate functions, are nevertheless unable to distinguish colours. The number of such persons is much more considerable than is generally supposed, and it is surprising that the majority of physicians and physiologists are ignorant of the existence of, or pay so little attention to, so common a fact.

It is known that every one can, in certain cases, receive abnormal sensations of colour; but it is only *in an intermittent manner and for a limited time.* Thus, whenever any one looks fixedly at a bright object placed on a surface of a dark tint, and then closes his eyes, or transfers them rapidly to another ground of a white colour, he immediately perceives an image more or less clear of the object beheld, but presenting a colour complementary to its own. Buffon has called this the phænomenon of accidental colours. It ceases at the end of a certain time, during which the primitive impression is seen in its turn to take the place of the secondary impression. It also arises when the eye, fatigued by the prolonged observation of a coloured and very bright object, looks at another object of a different colour. Various theories have been proposed to account for these coloured perceptions (which the Germans call *subjective*, and which Goethe terms *physiological*),—among others that of Scherffer†, for which Professor Plateau has recently substituted

* This Memoir had been communicated to the Société Vaudoise des Sciences Naturelles, March 5, 1840. (See *Actes de la Soc. Helvet. des Sciences Naturelles*, 1841, p. 194.) Its conclusions have also been pointed out (August 3, 1841) at the Meeting of the British Association at Plymouth. (See Report for 1841—Transactions of the Sections, p. 40. Silliman's American Journal, January 1842, tom. xlii. p. 62. *L'Institut* of February 3, 1842, No. 423, p. 47.) Numerous additions have been subsequently made.

† Dissertation on Accidental Colours.—*Journ. de Phys.* tom. xxvi. 1785.

a more rational one*. This case appears to be well known, and I have no occasion to dwell upon it here.

But there have long ago been ascertained facts of abnormal coloured vision in which *the affection is habitual and permanent.* These may be classed in two distinct categories:—

1. That of persons in whom *all* coloured impressions are constantly defective from a disordered condition. Some perceive the flame of a candle surrounded by an iris,—others think that all objects near them have a yellow, green or blue tint, &c. Their malady has been described by oculists under the name of *Chromopsis* or *Chrupsia*†.

2. The category of individuals incapable of distinguishing from one another a variable number of colours, as there are some who cannot distinguish the intervals of musical tones; they confound blue with violet, light blue with light green, dark green with brown, sometimes rose colour with light yellow, &c., always distinguishing the pale tints from those which are bright. The denominations of *Achromatopsis*‡, *Chromatopseudopsis*, *Chromatometablepsis*, *Akyanoblepsis*§, &c., have been employed by writers to designate the different cases which they have observed and described in a manner more or less confused.

* J. Plateau, *Mem. Ac. des Sci. de Brux.*, tom. viii. 1834. See also the remarkable memoirs of Professor Fechner in Pogg. *Ann. der Phys. und Chem.* 1840.—E. W. [See also the Lond. and Edinb. Phil. Mag., Dec. 1839, vol. xv. p. 441.—Ed.]

† The *Chrupsia* takes place in some cases of jaundice. Boyle relates that persons in the plague saw all objects, and even their clothes, as surrounded with rainbows (*Experimenta de Coloribus*, p. 1). Under the influence of a very lively fear, it is said that persons see gray or blue prevail in the external colouring. Dr. Parry mentions an old general who, in the evening before the candles were lighted, and in the morning for the first hour after he went out, imagined all white objects to be of a deep orange colour approaching to scarlet (Collections from the Unpublished Medical Writings of C. H. Parry, M.D., vol. i. pp. 560, 568, 569. Lond. 1825). Dr. Mackenzie mentions a person who saw all objects as if tinged with green, in consequence of a wound of the cornea with prolapsus of the nasal part of the iris (on the Diseases of the Eye, p. 862). Five persons having poisoned themselves with roots of henbane, were treated, some by *Tartar. stibiat.*, and the others by *Theriaca*; they were cured, but they saw for three days everything around them of a scarlet colour. (Letter of Dr. Patouillat in the Phil. Trans., vol. xxxix. p. 446. 1738.)

‡ *Achromatopsis*, properly speaking, is the absolute impossibility of distinguishing colours. Those who are affected with it in general see everything as gray: they are very few in number. According to Professor Jüngken, this imperfection occurs especially in individuals with gray eyes, rarely in those who have the iris brown; it dates commonly from the birth, and, in this case, it is hereditary and incurable; but it is manifested also gradually and as a symptom of cataract, of glaucoma and of amaurosis. (*Die Lehre von den Augenkrankheiten*, p. 841. Berlin, 1832.)

§ Goethe, *Farbenlehre*, tom. ii. p. 105.

I propose, in this Memoir, to cast a rapid glance over the principal facts of this second class hitherto known. Reserving the term *Chromopsis* for those cases in which colours are perceived in an extraordinary manner in consequence of a change of health, I shall apply to that in which the affection is natural the name of *Daltonism*, proposed by Professor Prevost, because the illustrious natural philosopher Dalton has described, as existing in his own case, many particulars of it*. I shall add a description of new observations made under very favourable circumstances; and, after a critical review of the explanations proposed by the various physiologists who have attended to this subject, I shall conclude with an enumeration of some consequences to which the study of it may lead.

It will perhaps be found that I have given too great an extent to the historical part of this work; but the absence of documents *in our language* on a subject so interesting, and the desire that the observations here recorded may save persons disposed to study the subject the labour of going back to the sources which treat of it, will, I hope, serve as my sufficient excuse.

* Professor Whewell is mistaken in attributing to me the choice of this denomination; I preserve it to avoid introducing a new one, whilst I quite agree with him, that few persons desire to be immortalized by their imperfections, and that Dalton, above all others, has no need of such a means of transmitting his name to posterity. (See Athenæum of August 28, 1841, No. 722, p. 699.) For the rest, I think with an illustrious natural philosopher (Sir D. Brewster), who has given a review of The Philosophy of the Inductive Sciences, written by the learned Master of Trinity College, that the term *Idiopts*, by which Mr. Whewell designates the Daltonians, is by no means a happy one. (Edinb. Review, January 1842, p. 266.) Nearly forty years ago the denomination *Daltonian* was employed in the oral instruction in the Academy of Geneva. Pierre Prevost printed as follows in 1827, in the *Bibliothèque Universelle*: "The subject, whose vision he has described, appears to differ from the great number of those whom I am accustomed to call *daltonians* only by a slight degree of darkness in the shades."—Tome xxxv. p. 321. And further on:—"On this statement.....I do not hesitate to pronounce him a *Daltonian*." —*Ibid.* p. 322.

[Note.—Sir David Brewster, in his remarks on this memoir (Phil. Mag. for Aug. 1844, p. 134), expresses his regret that the author should have continued to employ this term, which he censures as degrading to the venerated name of Dalton, and faulty in regard of nomenclature. It is with reluctance that the Editor becomes accessary to the retention of this objectionable denomination, for which he would have much preferred to substitute *Parachromatism*, *Parachromatic*, &c., derivatives of παραχρώννυμι, παράχρωσις, &c., as designating generally the fact of perversion of colour; but he is advised that such a change would be beyond the province of a translator. He has, however, ventured to add, in the title merely, the term Colour Blindness, adopted by Sir David Brewster. *Dyschromatopsis*, *Pseudopsis* and *Heteropsis* have been suggested; but the two latter are not sufficiently specific.—Ed.]

II.

Anterior Observations.

§ 1. *Of the Classifications.*

The facts of daltonism hitherto described are not very numerous. We find no mention of them in our best treatises of French physics (that of M. Péclet excepted), nor in the works of Priestley* and of Sœmmering†, nor in those of Burdach‡, of Tiedemann§, of Richerand‖, of Majendie¶, &c., on physiology. Professor J. Müller does not speak of it in his great Treatise of the Comparative Physiology of Vision in Man and Animals**, and in his 'Manual of Human Physiology'†† he only cites the observations of M. A. Seebeck, jun., which will be noticed hereafter. The interesting memoir of the latter‡‡, a work by M. Szokalski, which I have not succeeded in procuring§§, a chapter of the work of Mackenzie on the Eye‖‖,—these, with a few lines by Goethe, and two or three notices scattered in the 'Philosophical Transactions' and in the English journals of medicine and physiology, are nearly all that I have been able to collect for the purpose of tracing the history of my subject.

* Dr. J. Priestley. The history and present state of discoveries relating to Vision, Light and Colours, vol. ii. Lond. 1772. 4to.

† Sam. Thom. von Sœmmering. *Ueber einige wichtige Pflichten gegen die Augen.* 5e Aufl. Frankf. a M. 1819.

‡ Burdach. *Die Physiologie als Erfahrungswissenchaft, mit Beyträgen von Karl Ernst von Baer und Heinrich Rathke.* Leipz. 1835, 5 vols. 8vo.

§ Tiedemann. *Physiologie des Menschen.* 2 vols. 8vo. Darmstadt, 1830–36.

‖ Richerand. *Nouveaux Eléments de Physiologie.* 10e edit. Augmentée par M. Bérard aîné. 3 vols. 8vo. 1833.

¶ Majendie. *Précis Elémentaire de Physiologie.* 5e edit. Bruxelles, 1838. 8vo.

** J. Müller. *Zur vergleichenden Physiologie des Gesichtssinnes des Menschen und der Thiere.* 1 vol. 8vo. Leipzig, 1826.

†† J. Müller. *Handbuch der Physiologie des Menschen,* tom. ii. p. 392. Coblentz, 1838.

‡‡ A. Seebeck. *Ueber den bei manchen Personen vorkommenden Mangel an Farbensinn.* Pogg. *Ann. der Phys. und Chemie,* Bd. xlii. p. 177 (1837). I ought to say that this work, of the existence of which I was ignorant when this Memoir was presented to the Société de Genève, has been of great use to me in completing it for publication. M. Seebeck has been so obliging as to give me a copy of it, to which he had added specimens of coloured papers which he used in examining and classing a great number of daltonians.

§§ Its title is, *Essai sur les Sensations des Couleurs.* Bruxelles, 1840.—See *Bericht über die Fortschritte der Physiologie des Gesichtssinnes, in den Jahren* 1839 *bis Mai* 1842, *vom* Medicinalrath Dr. Tourtual zu Münster, p. lii. Müller's *Archiv für Anat. Physiologie und wissensch. Medicin* for 1842.

‖‖ W. Mackenzie. A Practical Treatise on the Diseases of the Eye. Lond. 1835, ed. 2. 8vo. chap. xx. p. 860.

The only observers who have attempted to classify the daltonians are MM. Seebeck, Szokalski and Purkinje.

M. Seebeck has arranged them in two divisions. The first comprises those individuals who are more deceived in the degree of colouring than in the nature of the colour. The tints which they confound more or less are,—light orange and pure yellow; dark orange, light yellowish or brownish green and yellowish brown; pure light green, gray, brown and flesh colour; rose red, green of a more blue than yellow tint and gray; crimson, dark green and chestnut brown; bluish green and dirty violet; lilac and blue gray; azure, blue gray and lilac gray. Their sense is very defective for the specific impression of *all* the colours in general; it is especially so for that of *red* and consequently for *green*, which is its complementary tint—colours which they distinguish little if at all from gray; it is further defective for *blue*, which they distinguish very incompletely from gray. Their appreciation of *yellow* is the most correct, although they often see less difference between it and the appearance of colourless bodies than is the case with the ordinary eye.

The second division comprises those persons who confound light orange, greenish yellow, brownish yellow and pure yellow; bright orange, yellow brown and grass green; brick red, rust and dark olive green; vermilion and dark brown; dark carmine and blackish blue green; flesh colour, gray brown and bluish green; dull bluish gray and gray a little brownish; dirty rose, somewhat yellowish, and pure gray; red rose, lilac, azure and gray passing into lilac; crimson and violet; dark violet and dark blue. They have only a feeble perception of the least refrangible rays: this is their most strikingly distinctive character. Lastly, yellow is the colour which they recognise best; they distinguish red objects a little better, and blue ones a little less, than colourless bodies, but above all reds from blues in a much less decided manner than persons of the first class *.

M. Szokalski has devoted an entire chapter of his work † to the examination of the defective cases of coloured perception, cases to which, with Sommer, he gives the general denomina-

* Seebeck, Mem. cit., p. 221. An extract from this excellent memoir has been inserted in the *Jahresbericht über die Fortschritte der anatomisch-physiologischen Wissenschaften, im Jahre* 1837, *von* Dr. Müller; Müller's *Archiv*, 1838, p. clxxiii. This extract has been republished verbally in the *Handbuch der Physiologie* of the same author.

† Müller's *Archiv*, 1842.

tion of *Chromato-pseudopsis*. He distinguishes five classes of them :—

1. That of persons in whom the sense of colours is almost completely wanting, and who, in place of the elementary colours yellow, red and blue, see only different degrees of white and black.

2. That of persons who also distinguish yellows :—external objects appear to them coloured with shades which generate the different mixtures of yellow, of white and of black.

3. That of persons who not only see yellow, but are besides capable of a particular perception, and the same for blue and for red ; these are the *Akyanopes* of Goethe.

4. That of persons destitute solely of the perception of red, which appears to them ash gray.

5. That of individuals who distinguish all colours, but not in a decided manner; instead of being able to distinguish the mixture of two colours they never see but one of them.

Prof. Purkinje divides daltonism into four varieties, which he names *Achromatopsis*, *Chromatodysopsis*, *Akyanoblepsis*, and *Anerythroblepsis*. The first two relate more to the intensity, the others to the nature, of the imperfection*. The same skilful physiologist has remarked that the latter also occurs in eyes in the normal state, when, the visual axis having a determinate direction, any coloured object is slowly introduced into the field of vision from its most outward boundary†.

The various ancient and recent observations which I have to relate appear to me to confirm the division of M. Seebeck, rather than that of MM. Szokalski and Purkinje. It would be very advantageous to make a strict classification of the daltonians, because for each category means might be offered at once sim-

* *Encyclopædisches Wörterbuch der medicin. Wissenschaften, herausgegeben von den Professoren der medicin. Facultät zu Berlin*, Bd. i. p. 259.

† *Beobachtungen und Versuche zur Physiologie der Sinne*, Bd. ii. p. 15. We also know that in certain circumstances both eyes do not see the same colours, if one of them receives laterally a bright light, from which the other is protected by a screen. The following, among others, is an experiment not mentioned in our treatises, and which would nevertheless deserve to be generally known. I take it from the *Positions de Physique* of M. Quételet[a] :—" Hold a leaf of white paper at a foot distance from you, and look at an object placed further off, but so as still to see the paper, which appears double. The flame of a taper is then to be brought laterally near to one eye, and to be prevented by a screen from acting upon the opposite eye; the paper then appears *red* to the last eye and green to the first; it is white at the parts where the two images encroach upon one another. On rapidly bringing the light from the opposite side, you see the phænomena reproduced in an inverse direction : that which was red becomes insensibly green, and *vice versâ*."—Tome iii. p. 175, 2e edit.

[a] [See an account of this experiment of Mr. Smith of Fochabers in the Phil. Mag., Series 3, vol. i. p. 249, and vol. ii. p. 168.—Ed.]

ple and few as palliatives of their imperfection; unhappily such an undertaking does not seem possible, and we may say that there are as many varieties of daltonism as of individuals who are affected with it.

I prefer, in consequence, to throw aside every systematic notion which may not have in its favour a sufficient proof, and only to separate the cases of *dichromatic* daltonism and of *polychromatic* daltonism, that is to say, where there are more than two colours perceived normally. With regard to the very rational distinction which M. Seebeck has the merit of having first established between the errors of appreciation of *intensity*, and those of judgment of the *individual kind* of colours, it is to be regretted that we cannot make it in the great majority of the descriptions which writers have transmitted to us. We must content ourselves with recommending it to those physiologists who may be engaged upon this complex subject.

I add, lastly, in favour of my opinion, that there exist a great number of different degrees in daltonism. When there are only two colours perceived, they commonly are reduced to a vague sensation of light and darkness: the influence of the red rays is almost null. But from this point to the case in which there are only errors in the appreciation of tints equal in brightness and approaching in colours—errors which only occur in artificial light, and which constitute the extreme limit of daltonism,—the number of intermediate degrees is undetermined and perhaps unlimited*.

§ 2. *Cases of Dichromatic Daltonism.*

The most ancient of those which have been described was related by Dr. Dawbeney Tubervile† in 1684. He says that a

* It is this great number of varieties of daltonism which appears to me an objection against the proof which Sir David Brewster has thought he found in this anomaly in support of his theory of three elementary colours (Edinb. Journ. of Science, N.S., vol. v. p. 19. *Bib. Univ.* tome l. p. 147). It cannot be said that "the physiological fact and the principle of optics on which he founds his analysis of the spectrum are perfectly in accordance and confirm one another." [On this Sir David Brewster remarks (Phil. Mag. Aug. 1844, p. 138), "What Prof. Wartmann calls my *theory of three elementary colours* is a *fact* as rigorously demonstrated as any physical truth can be; but if he does not admit it as *true* over the whole length of the spectrum, he cannot avoid, if he makes the experiments, admitting it as true over the greater part of it; and this is all that is necessary for my present argument."—Ed.]

† Two letters from the great and experienced oculist Dr. Dawbeney Tubervile of Salisbury, to Mr. William Musgrave of Oxon, containing several remarkable cases in physic relating chiefly to the eyes.—Phil. Trans. No. 164, p. 736 (Aug. 4, 1684). Lowthorp's Abridgement, vol. iii. part 1. p. 40.

young woman 32 or 33 years old, came to consult him about her sight, which, although excellent in other respects, incapacitated her from appreciating any other colour than white and black, although she could often read for nearly a quarter of an hour in the greatest darkness.

This last circumstance, which is very extraordinary, appears to be rather frequent with daltonians. We shall find several instances related, especially by English physicians, such as Dr. Colquhoun and Dr. Nicholl. Spurzheim* mentions a family all the members of which could only distinguish black and white.

Mr. Huddart† mentions a man named Harris, a shoemaker at Maryport in Cumberland, who distinguished in colours only tints of luminous intensity, calling all bright tints white and all dull ones black. He one day found in the street a child's stocking, and was much surprized at hearing it called red, whereas he himself thought he had defined it completely by calling it a stocking. This circumstance revealed to him the imperfection in his sight, and made him understand why his little companions perceived something else besides a difference of form and position between the leaves and the fruit of the cherry-tree. Two of the brothers of Harris had the same imperfection as he, whilst two other brothers, his sisters and his relations, had a normal vision.

§ 3. *Cases of Polychromatic Daltonism.*

Mr. Harvey‡ mentions a tailor at Plymouth who perceives in the rainbow and in the spectrum only two tints, yellow and light blue. The only colours which he distinguishes exactly are white, yellow and green. It is said that he one day sewed a scarlet piece on to a pair of black silk breeches. Black appears to him in general green, sometimes crimson; blue appears dark blue, crimson or black; violet is blue, unless it is very bright; green is black and brown; carmine, red lake, crimson appear blue; brown appears green; the dark orange tints are brown, and the light ones are yellow.

Sir J. Herschel§ mentions a distinguished optician (Mr.

* G. Spurzheim. Phrenology, 3rd edit. p. 276. J. De Ville. Manual of Phrenology. London, 1835, p. 108.

† An account of persons who could not distinguish colours, by Mr. Jos. Huddart, in a letter to the Rev. Jos. Priestley (London, Jan. 15, 1777).—Phil. Trans., vol. lxvii. p. 260.

‡ Edinb. Phil. Trans., vol. x. p. 253. Phil. Mag. S. 1. vol. lxviii. p. 205. Edinb. Journal of Science, vol. v. p. 114. *Bib. Univ.*, tome xxxv. p. 175.

§ Article 'Light' in the *Encyclopædia Metropolitana*, § 507, p. 345. *Traité de la Lumière*, traduit par MM. Quételet et Verhulst, tome i. p. 305.

Troughton), who had lost an eye by an accident, and whose other eye perceived a sensation of brightness in all parts of the spectrum, but distinguished in it only two colours, blue corresponding to the most refrangible rays, and yellow to those which are the least so. Experiments in confirmation have been made by means of polarized light, which traversed a moveable lamina of mica, and which gave simultaneously two colours, the one complementary of the other, and whose coloration differed according to the inclinations of the crystal. According to Mr. Whewell, all the male members of the Troughton family are similarly affected*.

The most interesting investigation to be noticed on this subject is that of the illustrious Dalton, who has described the affection which we are considering in his own case and in that of some of his pupils. The vast extent of Dr. Dalton's knowledge is a guarantee of the fidelity and care he has exercised in analysing his sensations, and renders the sketches of them which he has published† very valuable. Dr. Dalton sees in the solar spectrum three colours only, yellow, blue and purple‡. The first two form a contrast, the last two seem to differ rather in degree than specifically. Rose colour seen by day appears sky blue a little weakened; in artificial light it takes an orange or yellowish tint, which contrasts strongly with the blue. Crimson is, by day, a dirty blue, and crimson wool a purple. Red and scarlet become by candle-light more brilliant and more vivid. By daylight Dalton perceives no difference between the red of a stick of sealing-wax and grass green; he calls the carnation of a ruddy complexion dark blue, and he assorts crimson with the colour of bright red, wine or mud, rose colour with light blue, brown with red, and gray with green. Lastly, on all points where he has a peculiar perception, the difference is less by candle-light than in sun-light.

Mr. Whewell relates §, that having asked Dalton to what ob-

* Athenæum, *loc. cit.*

† Extraordinary facts relating to the Vision of Colours, with observations, by Mr. John Dalton; read Oct. 31st, 1794.—Memoirs of the Literary and Philosophical Society of Manchester, vol. v. part 1. p. 28. 1798.

‡ Sir D. Brewster affirms, on the contrary, in his 'Letters on Natural Magic,' that according to his observations, Dalton saw the whole entire spectrum, but that the red portion appeared to him yellow. (Page 27 of the French translation.)—E. W. [There is no contrariety whatever between Sir D. Brewster's affirmation and Dr. Dalton's own statement; Dr. Dalton has never stated that the spectrum he saw was *shorter* than the spectrum seen by others.—Ed.]

§ Athenæum, *loc. cit.*

ject he should compare his doctor's robe, which was of a brilliant scarlet, the latter pointed to the trees, and declared that he perceived no difference between the colour of his dress and that of their foliage.

Goethe* says that he knew two young men under twenty years of age whose sight was very good, and who appreciated with much delicacy the gradations of light and dark. They saw like us the white, black, gray, yellow, and reddish-yellow; they called carmine dried in a thick layer red; but they called the colour of a thin touch of carmine made with a brush on a white shell blue, as well as that of the petals of the rose. They confounded the rose and the blue with violet, and these colours appeared to be distinguished from one another only by small shades of brightness, darkness, of liveliness or faintness.

Professor Péclet† mentions two brothers to whom carmine, violet and blue seemed identical; they called the colour of the peroxide of iron green, and confounded the madder-red of the trousers of the troops of the line with the green of the trees. In their sight yellow had a great brilliancy. These results were obtained by making them determine the different colours with which strips of paper had been covered.

Dr. Sommer has carefully described the peculiarities of his daltonism‡. In brief, he could not appreciate red and its mixtures, but he distinguished yellow, black, blue and white. His brother and three other persons were similarly circumstanced.

Phrenologists have also paid attention to some cases of daltonism. Dr. Combe of Edinburgh relates the following details of Mr. James Milne, a brass-founder in that city§. His maternal grandfather was a daltonian, confounding brown with green. His two brothers and Mr. Spankie, his second cousin, see like him; whilst his father, mother, maternal uncle and his four sisters have a normal organ. Mr. Milne does not distinguish brown from green, blue from rose-colour, the colour of grass from that of the orange; purple, indigo and violet appear to him only different tints of the same colour. In the rainbow he sees distinctly only the yellow and blue; he perceives other stripes, but he cannot name them. He calls crimson blue by

* *Zur Farbenlehre*, in the chapter *Pathologische Farben*, §§ 104–113.

† E. Péclet. *Traité Elémentaire de Physique*, tome ii. p. 362, 3e edit. 1838.

‡ Græfe und Walther's *Journal für Chirurgie*, Bd. v. Heft 1. p. 135.

§ Combe's System of Phrenology. Transactions of the Phrenological Society, p. 222. Chambers's Edinb. Journal, vol. iv. p. 118.

day, and bright red by candle light. For the rest, he distinguishes very well black from white.

Dr. Nicholl has recorded the examination of two remarkable daltonians. One*, a child eleven years old, did not call any colour green; he called dark green, brown; light yellow, yellow; dark yellow and light brown, red; pale green, light red; light red and rose-colour, light blue; the red, red; light blue and dark blue, blue. The solar spectrum presented to him only red, yellow and purple. His mother and his four sisters had their sight correct, but that of his maternal grandfather and some brothers of the latter was imperfect.

The second subject studied by Dr. Nicholl† was a man aged forty-nine. Like the preceding, he had gray eyes and a yellow tint around the pupil. He cannot distinguish green from red. He perceives scarlet colour, but he calls dark green brown; light yellow, yellow; dark yellow, light brown; light red, rose and violet, blue; he appreciates very well dark blue and black. The rainbow appears to him yellow in the centre and blue toward the edges; crimson curtains appear to him blue by day and red by candle-light. To his eye grass is red, and red fruits are of the same colour as the leaves of the trees which bear them. He has not a clear notion of the complementary colours. Lastly, he sees further and more distinctly in the dark than his relatives and friends.

Dr. Colquhoun has also described two cases very well characterized‡. The first is that of an educated person, who has a decided taste for paintings, and has himself described the peculiarities of his vision:—"I ought to state at the outset, that I do not invariably confound the colours to the distinction between which my eye is generally insensible. Thus the brilliant reds and greens in the plumage of certain birds, and in some fruits, I can always appreciate with perfect accuracy, whilst to the generality of eyes the difference between such colours and those which I am certain to confound is not perceptible; neither can I myself explain in what the peculiarity consists, which thus enables me to appreciate their quality truly.

* Account of a case of curious imperfection of Vision, by Whitlock Nicholl, Medico-Chirurgical Transactions of London, vol. vii. p. 477.

† Account of a case of defective power to distinguish colours, by Whitlock Nicholl of Ludlow, Medico-Chirurg. Trans. of London, vol. ix. p. 359.

‡ Glasgow Medical Journal, vol. ii. p. 12, 1829.—I am indebted to the kindness of Dr. Coldstream of Leith for the manuscript communication of this article, inserted in a collection very rare on the Continent.

"The colours between which I have the most difficulty in distinguishing the difference are, in the first place, those reds which approach nearest to scarlet, and the yellower greens, such as the leaves of the lime-tree, the birch, the elm, &c. When blue is added to scarlet, even in a minute proportion, I perceive the original scarlet is changed; but when the same proportion of blue is added to the tint of green with which I am apt to confound scarlet, I am unable to distinguish the difference between this bluer green and the scarlet to which blue has been added.

"I am also apt to confound dark or rather deep green and black, and the deeper shades of brown; .... as also gray with pale green, or pale red of the same depth of tint.... It has been suggested to me that this seeming defect of vision was ideal, and that it arose from a carelessness in naming colours on my part; but this certainly is not the case, for I have made many trials on the subject, which with me were quite decisive. Thus, I cannot perceive a bit of red sealing-wax if thrown down upon the grass, nor a piece of scarlet cloth hung upon a hedge, which I was told was to be seen a mile off. I once gathered some lichen, as a great curiosity, from the roof of a friend's fishing-house; I thought it was of a bright scarlet, from its seeming to be of the same colour as the tiles; in reality it was of a bright green..... Upon another occasion I perceived no difference in the complexion of a foreign lady who had purposely substituted Prussian blue for her rouge..... Nothing in my sight contrasts more with black than the azure hue of the atmosphere. I also see much better far off than near, owing to the interposition of a wider stratum of air. So much is this the case with me, when viewing a distant object, as to overcome the effect of perspective; and the shading in the form and garments of persons at a distance is often so predominant as to overcome the effect of diminution of size; and although I see the object most distinctly, I am unable to tell whether it be a child near me or a grown person at a distance, &c. By candle-light all yellows appear to me white; crimson seems scarlet; pale green, blue; orange of a dirty red. I am not aware that any of my relations have the least peculiarity of vision."

The other case is that of an orchardist in Clydesdale, aged about fifty years. His eye is perfectly formed; the iris is a bluish-gray, and the pupil is surrounded with a narrow dark yellow circle. He discovered his imperfection by the inability to distinguish certain fruits as they hung on the tree. His first trade

was that of a weaver, but he gave it up, because he confounded the red, black, green and purple threads. In the rainbow he only discerns the yellow and blue; nevertheless he indicates its form correctly, and was one day the first to point out a comparatively feeble secondary arc. He much more commonly recognises persons by their voice than by their features. Not one of his numerous children, nor of his relatives in the ascending line, is a daltonian. The principal characters of his vision are the following:—

In open day he confounds all the tints of white; he names correctly the yellow and its varieties; calls orange an intense yellow, but does not see in it any mixture of red; he hesitates as to the pale tints, which he designates as yellows, reds, browns, or even drabs, and cannot assign any name to the very dark shades; he confounds red with lilac, rose, brown, black, white, although he perceives the difference of the light tints and dark tints; he has but very confused notions of green, which he thinks to be white, lilac, yellow, blue, or black; he is scarcely at all deceived in the blue, but extends the denomination to violet; lastly, he cannot ever characterize either brown, or gray, which he calls lilac, or even the darkest black. In bright candlelight he sees white, gray, yellow and green as by day; he recognises orange well enough, but calls the dark reds and dark blues black; the light blues, blues and rose-colours; he cannot specify the shades of violet and brown, nor those of black, which he takes for brown, red, green or black.

Lastly, we are indebted to Prof. Seebeck for the account* of twenty-one cases of daltonism, fifteen of which have been studied with great sagacity. I shall not enter into the detail of his observations; the conclusions which he draws from them, and which have been related above, render this the less necessary, as there is scarcely any peculiarity of which the cases previously described do not offer examples. I shall confine myself to the relation of the most striking traits of the vision of a daltonian of his first class †.

He is a young man eighteen years of age, who calls greenish-blue and lilac, blue; bluish-green, pure gray, lilac-gray, rose-colour, violet-rose and light blue passing into gray or greenish, green; the yellow, orange, reddish-yellow, light yellowish-green, yellowish-brown, and rust-brown, all red; the dark yellowish-red and dark grass-green, brown; the crimson, dark violet, dark blackish- or bluish-green and the brown, red or brown: green

* Mem. cited. † Mem. cited, p. 180.

and red are the most indistinct to him; moreover, he does not say freely that a tint is gray or yellow*. Blue and yellow are what contrast most forcibly to his eye. He judges very incompletely of the opposition of colours. He distinguishes three fundamental colours, which he calls green, blue and red; the last appears to him brown when it is deep. This daltonian sees the limits of the spectrum as we do. He confounds blue with violet and with a slightly bluish-red, more in the colours produced by the prism or by interferences than in those of opake substances.

§ 4. *Cases of Daltonism incompletely described.*

Besides the facts which I have just related, there are a small number of others which are recorded in various works, but with too few details to render it possible to characterize them well. The following are the principal among them:—

Mr. Scott† informs us, that a full red and full green, pale blue and pink, deep red and blue gave him the same sensation, whilst he easily distinguished yellow and deep blue. He called the claret colour of a garment deep black. The same imperfection existed in his father, his maternal uncle, one of his sisters, and the two sons of the latter.

Gall‡ states that Dr. Unzer of Altona could never distinguish green from blue.

Rozier § speaks of an individual whom a similar vision prevented from devoting himself to painting; he used red instead of deep blue. Helling‖ mentions a person who confounded light blue with green and red.

Dr. Butter¶ describes the daltonism of a young man, R. Tucker, aged nineteen. To this person the red of the spectrum appeared brown; the orange, green; the yellow, orange; the blue, pink; lastly, the indigo and violet, purple.

* M. Seebeck remarks, that all the persons whom he examined confounded the colours with gray,—an important fact, and one which had not hitherto been noticed.

† An account of a remarkable imperfection of sight; in a letter from J. Scott to the Rev. Mr. Whisson of Trin. Coll. Cambridge; communicated by the Rev. Michael Lort.—Phil. Trans., vol. lxviii. p. 611 (1779).

‡ Gall. *Anatomie et Physiologie du Système Nerveux*, tome iv. p. 98. Spurzheim, *op. cit.* p. 276. De Ville, *op. cit.* p. 108.

§ Rozier. *Observations sur la Physique*, tome xiii. p. 86.

‖ Helling. *Praktisches Handbuch der Augenkrankheiten*, Bd. i. p. 1.

¶ Remarks on the Insensibility of the Eye to certain colours, by John Butter, M.D., Edinb. Philos. Journal, vol. vi. p. 135 (1822). Transactions of the Phrenological Society, p. 209. Combe's System of Phrenology.

Sir D. Brewster* instances a person, still young, and who saw in the spectrum only yellow and blue. When the middle of the red space was absorbed by a blue glass she saw the black part terminated on both sides by what she called yellow.

M. Collardo confounded blue with yellow, red with green†.

Girod de Chantilly speaks, among others‡, of an apothecary of Strasburg who with difficulty distinguished colours. He explains this anomaly by admitting that there are only three colours, and that the retina possesses for the perception of each of them a peculiar membrane, which may in certain cases become inactive.

Brandis§ relates of himself, that he cannot distinguish light blue from rose-red, that he easily confounds green with blue, yellow with red, yellowish red with green in its deep tints, blue with red in its light tints. His nephew had been obliged to give up a silk trade because he could not distinguish sky-blue from rose-red.

Wardrop‖ remarks that daltonians perceive a difference in colours in general, but without being able to say in what it consists, or to name the colours separately. According to him, they are never mistaken in yellow and blue; all the other colours appear to them to be modifications of these. They see in the spectrum only yellow and blue. They distinguish with difficulty the different kinds of green and red; they call vermilion, the colours next to yellow, carmine, and other similar tints, which they however find yellow by candle-light, blue. It is evident that the author has studied but a very limited number of cases of daltonism.

III.

New Observations.

§ 1. *General Remarks.*

Number of Daltonians.—I have already said that the number of persons affected with daltonism is much more considerable

* Brewster. Edinb. Journ. of Science, vol. vii. p. 85. A Treatise on Optics, chap. xxxvi. p. 311. (vol. xix. of the Cabinet Cyclopædia. Lond. 1838.)

† *Journ. de Phys.*, tome xii. p. 86.

‡ In a work published in English under the pseudonym of G. Palmer, afterwards translated into French with the title of *Théorie des Couleurs et de la Vision*, 8vo.

§ Goethe. *Zur Naturwissenschaft und Morphologie*, 1 Heft, p. 297.

‖ Essays on the Morbid Anatomy of the Human Eye. London, 1818, vol. ii. p. 196. Meckel's *Archiv für die Physiologie*, Bd. v.

than is generally imagined. Professor Seebeck found five out of forty youths who composed the two upper classes in a gymnasium at Berlin. Professor Pierre Prevost declared that they amount to one in twenty. I do not think that this estimate is much exaggerated, for I have readily found a number of persons affected with this singular anomaly. It is necessary to remark that daltonians often are themselves ignorant of the imperfection of their vision. We may add, however, that we do not find in ancient authors any passage which can be referred to daltonism, and that the numerous travellers who have gone over the old and the new world are quite as little explicit in this respect. Are we to conclude from hence that this imperfection is the lot of modern European nations? It is infinitely more probable that in other regions and in past ages the spirit of observation less mature has not discovered it.

Characteristic Signs.—Is there any means of deciding by simple inspection of the visual organ of any one, whether he is or is not a daltonian? This question is very important, for it is not rare to meet with persons devoted to painting or to other professions from which the state of their perception of colours should have excluded them. I would not venture to affirm that the answer should be *in all cases* negative. I have observed, in fact, that the daltonians whose eyes are brown, of the colour which the English call hazel (*noisette*), present, under an incidence more or less oblique, a golden lustre of a peculiar tint. Dr. Nicholl has pointed this out in the cases of the young child and of the oldest man that have been related above, and Dr. Colquhoun mentions it in the eye of the gardener of Clydesdale. Miss Sedgwick says of M. de Sismondi, that he had *brilliant hazel eyes**; the illustrious historian was affected with daltonism. Struck with this lustre in the eye of a young student of the age of fifteen, I subjected him to some trials, which showed, according to my prediction, his inaptitude, until then undiscovered, for distinguishing different colours. The eyes of M. D***, of which I shall have to speak hereafter, presented the same peculiarity. I am, however, far from attributing much importance to this remark.

It has been asserted that there are more daltonians with blue than with black eyes. This assertion cannot be sustained; amongst the persons whom I have examined, the great majority belonged to the second category. On reckoning up all the ob-

* Letters from Abroad to Kindred at Home, vol. i. p. 250.

servations of daltonism known to me, in which the colour of the iris has been noted, I find that the two tints are in equal numbers. M. Seebeck also rejects this opinion, which is founded on the fact that the majority of the cases examined have been in Germany and England, where blue is the prevailing colour of the eyes.

Division according to Sex.—Daltonism is much more common among men than women. I was told of a lady who confounds colours, but I have not had an opportunity of examining in what the defect of her sight consists. The same is the case with a sister of D***; two women mentioned by M. Seebeck*, and two cases cited by the English, but one of which is doubtful†, are the only ones, in nearly 150 registered observations, which do not relate to the male sex. If it be true that the works of the needle are the means of perfecting a delicacy in the judgement of tints, and that in women the organ of colour is more developed than in men, as Gall asserts, it is worthy of remark, that these very works ought to lead daily to the detection of cases of daltonism in the female sex, if these cases were numerous.

Influence of age and kindred.—Daltonism ordinarily dates from the birth. I know but two exceptions to the very great generality of this rule,—that of M. D***, to which I shall recur, and that of a young man of seventeen, mentioned by M. Seebeck‡, who had suffered from an inflammation of the eyes from his infancy, and who had retained from this cause a weakness of sight; but his daltonism can scarcely (*schwerlich*) be dated from that period.

With respect to affinity, there are some daltonians no one of whose kindred exhibits this anomaly of vision; others have, so to speak, inherited it from their father or their uncle, either paternal or maternal (without, in the latter case, the aunt participating in it); lastly, it is not rare to find brothers, several of whom are daltonians, without their being all necessarily so. The sisters are almost always privileged, as we have seen.

§ 2. *Details of two Observations.*

The majority of my own observations approach too nearly to those which I have enumerated for it to be of use to give them

* Mem. cited, p. 232.

† Phil. Trans., vol. lxviii.; and Medico-Chirurg. Trans. of London, vol. ix. It is this last case which presents uncertainty.

‡ Mem. cited, p. 200.

in detail. I shall confine myself to the citation of one of them entire, adding another which has been communicated to me.

The most interesting case which I have studied is that of M. Louis D***, born at Locle, July 22nd, 1810. He is the eldest of seven brothers and four sisters. His parents have a normal sight, and their children are assorted in a very singular two-fold category. The first is formed of those who have red hair and who are not daltonians; the second, of whom D*** is one, is composed of those whose hair is blond and whose vision is anomalous as to colour: each sex has representatives in each of these two divisions.

D*** attests, according to his own recollection and the evidence of his mother, that in his infancy he perceived colours in the ordinary manner. Put to boarding-school at a very early age in the Canton of Berne, he returned at the end of two years without very distinct notions of their diversity, and thus reached his ninth year. He at that time received a hard blow on his head, so violent that the skull was fractured; the treatment of the wound rendered surgical operations necessary, some of them on the back, after which his perception of colours became defective. The fact, however, that three of his brothers are similarly affected, without having been placed in the same circumstances, takes from this pathological observation a great part of its importance.

His father endeavoured, by repeated corporal punishment, to put a stop to what he called a perverse pretence, and D*** remembers the correction which his master, a bookbinder, one day inflicted on him for having used red paper for some books the cover of which should have been green.

I have subjected this daltonian to a great number of experiments, varied so that they should mutually check one another. I had, in fact, to guard against errors arising from faulty indications on his part, and attributable to the education which his habitual relations compulsively give him. Moreover he did not disguise his repugnance to reply to precise questions on points where the absence of the perceptive faculty involves, as is known, that of the corresponding ideas, which no external process of instruction can supply the place of.

D*** does not perceive any great difference between the colour of the leaf and that of the ripe fruit of the cherry; he confounds that of a paper sea-green with the scarlet of a riband

placed close to it*. The flower of the rose seems to him greenish-blue, and he calls the ash-colour of the quick-lime (*chaux vive*) of commerce light green †.

I presented to him successively papers shaded with different tints, requesting him to assort those which appeared to him similar. I instantly perceived that the influence of the surface more or less glossy of the paper, and the glare which results from this, prevented his stating with certainty, and I gave up this mode of experiments, in which the judgements of the sight were in a manner modified by those of the touch ‡.

I wished to know what effect the sight of a solar spectrum would produce on him. I operated by means of a good prism, in very favourable weather and in a dark chamber, on the 7th of May 1839, between 9 and 10 o'clock in the morning. The coloured bands received on a screen of white paper were brilliant and distinct; they extended a length of about $0^{m}{\cdot}102$. D *** perceived four colours only, the blue, green, yellow and red. He limited the blue part exactly to the space occupied by the violet, indigo and blue; he called the green and yellow bands less an interval of $0^{m}{\cdot}002$ towards the orange, green; he called that band of $0^{m}{\cdot}002$ and a fraction of the red $0^{m}{\cdot}012$ in breadth, yellow; lastly, the remaining $0^{m}{\cdot}008$ of red appeared to him of a red difficult to define, although certainly a red §.

These anomalies in the perception of reflected colours once known, it remained to verify them for refracted light. I employed, for this purpose, thirty-seven plates of glass differently coloured, and I wrote down, from the dictation of the daltonian, the different impressions which he experienced on placing each of them in succession between the sky and his eye. I repeated these trials several times, in order not to leave the results ques-

* I have observed a like circumstance in another daltonian, M. Mary of Metz. He could not perceive a young peasant girl clothed entirely in red, and who crossed a meadow, the green colour of which had taken the deep tint which is common some instants after sunset.

† Professor M *** of Zurich is similarly circumstanced, &c.

‡ I have remarked, like M. Seebeck, that the judgement passed by daltonians on colours is less positive and less exact for opake media than for transparent substances.

§ I have already said that many dichromatic daltonians see better in a demi-obscurity than other persons whose sight is more piercing by day than theirs; the same is the case with D ***, and two other persons whom I examined. Does not this proceed, as M. Seebeck presumes (Mem. cit., p. 224), from the fact that the less refrangible rays being the first to disappear in twilight, the diminution of the glare of light is more sensible to ordinary eyes, which perceive these rays better than they?

tionable from indications carelessly given; they were all made in calm weather and in sunlight, both before and after noon. I have given in Table I. a detail of one of them, performed on March 2, 1840, between 3 and 4 o'clock, with a grayish-blue sky. The glasses are there classed in the order of decrease of their tints to my eye; they comprise the seven primitive colours more or less pure, with some of their combinations, but do not present that fusion by insensible degrees which is remarked in those of the solar spectrum.

TABLE I.

Experiments with Plates of Coloured Glass.

Nos. in order of the observations.	Nos. of order of the plates.	Colours according to my vision.	Colours according to the vision of a Daltonian.
1	27	Very dark red.	Very obscure black red, indiscernible.
2	1	Less deep red.	Very deep red brown, indiscernible.
3	2	Less deep red.	Red.
4	37	Less deep red.	Light red, of combustion.
5	26	Less deep red.	Lighter red, or dark yellow.
6	20	Deep orange.	Lighter red, bright, indistinct.
7	35	Less deep orange.	Very bright yellow, indistinct; red?
8	34	Less deep orange.	Flame-coloured yellow, indistinct; golden red.
9	16	Less deep orange.	Fine red, light.
10	15	Deep yellow.	Light red; yellow? [the 2nd plate.
11	3	Less deep yellow.	Lighter red, and more brilliant than that of
12	4	Less deep yellow.	Yellowish red, indistinct.
13	5	Less deep yellow.	Red of combustion.
14	21	Less deep yellow.	Light green.
15	17	Less deep yellow.	Very light green.
16	6	Deep green.	Bluish green } equal colours and not distinct.
17	7	Less deep green.	Bluish green }
18	22	Less deep green.	Fine green.
19	30	Bluish green.	Light green. [the 6th and 7th plates.
20	8	Green, lighter than No. 22.	Green less deep and less reddish than that of
21	11	Deep blue.	Greenish blue.
22	10	Less deep blue.	Blue.
23	36	Less deep blue.	Light blue.
24	13	Less deep blue.	Lighter blue.
25	14	Less deep blue.	Lighter blue than that of plate 13.
26	28	Blue, ill-defined.	Weak blue.
27	12	Dirty blue, less distinct.	Fine blue, lighter than that of plate 11.
28	32	Deep indigo.	Deeper blue than that of plate 28.
29	9	Less deep indigo.	Deep blue.
30	33	Less deep indigo.	Fine blue, lighter.
31	23	Deep violet.	Fine deep blue.
32	29	Less deep violet.	Deep blue.
33	24	Less deep violet.	Deep blue.
34	31	Less deep violet.	Deep blue.
35	25	Less deep violet.	Fine blue, weaker.
36	18	Less deep violet.	Light blue, like that of plate 13.
37	19	Less deep violet.	Fine sky-blue

This table shows, notwithstanding some doubtful appellations, the evident confirmation of the results obtained with the solar spectrum. The thirty-seven plates of glass exhibit to the eye of D*** only four different colours, if we except varieties of intensity; only here there are some changes in the name of the orange tints and in that of the red and yellow tints which approach the nearest to them. The shades which he has a difficulty to characterize and which he names sometimes reddish, sometimes yellowish, are precisely those which are a mixture in different proportions of yellow and of red.

However accordant these trials were, I thought that it would be useful to verify them by others, in which I should employ pure tints produced by phænomena of coloured polarization*. This method appeared to me more sure, because the glasses I had employed might present at different places differences of thickness or coloration, sometimes also striæ which have an influence on a very clear refraction of light, and thus introduce into delicate researches chances of error which it was important to avoid.

With this view I made use of an apparatus invented by M. de Norrenberg. After having disposed the glasses in a convenient manner, I placed on the stand a quartz perpendicular to the axis $0^{m}{\cdot}002$ in thickness, and on the opening of the graduated circle a Nichol's prism. The observations were made on Thursday, December 5th, 1839, in snowy weather, at half-past 2 P.M. The readings took place from 5° to 5°, starting from 90°, placed at the right of the observer, and with whom we commenced by making the mark coincide. In Table II. I give the indications of D*** for the circles right and left as well as my own made immediately after. I am indebted to the kindness of Mr. Taylor, formerly student of the University of Cambridge, for checking the results which I have put down.

[* Sir John Herschel, in his 'Treatise on Light,' has given a similar series of experiments made by himself on the eyes of the late Mr. Troughton.—Ed.]

TABLE II.

Experiments with Polarized Light.

Nos. of order of observation.	Degrees of the circle.	Colours according to my sight.		Colours according to the daltonian.	
		Circle—right.	Circle—left.	Circle—right.	Circle—left.
1	90°	Blue.	Greenish yellow.	Blue.	Straw yellow.
2	85	Lighter blue.	Deeper greenish yellow.	Lighter blue.	Darker yellow.
3	80	Lighter blue.	Deeper greenish yellow.	Lighter blue.	Darker yellow.
4	75	Lighter blue.	Deeper greenish yellow.	Lighter blue.	Lighter yellow.
5	70	Lighter blue.	Brown yellow.	Lighter blue.	Light reddish.
6	65	Lighter blue.	Chocolate brown.	Lighter blue.	Fine red.
7	60	Whitish blue.	Lilac brown.	Bluish white.	Finer red.
8	55	Bluish white.	Purplish lilac.	Undecided white.	Undecided blue.
9	50	Yellowish white.	Lilac purple.	Dull white.	Deep blue.
10	45	Whitish yellow.	Fine violet.	White less dull.	Blue like No. 9.
11	40	Light straw yellow.	Lapis lazuli blue.	Fine white.	Like No. 9.
12	35	Darker straw yellow.	Less deep blue.	Yellowish deal wh.	Like No. 9.
13	30	Straw yellow.	Cobalt blue.	Yellowish.	Lighter blue.
14	25	Deeper yellow.	Lighter blue.	Fine yellow.	Lighter blue.
15	20	Deeper yellow.	Lighter blue.	Fine yellow.	Lighter blue.
16	15	Deeper yellow.	Lighter blue.	Greenish yellow.	Lighter blue.
17	10	Brass yellow.	Sky azure.	Orange yellow,	Lighter blue.
18	5	Lemon yellow.	Hazy blue.	Yellow.	Lighter blue.
19	0	Dull deep lemon.	Dull grayish blue.	Dead yellow.	Very light blue.
20	5	Deep dirty yellow.	Grizzle blue.	Greenish yellow.	Lighter blue.
21	10	Light brown yellow.	Gray blue.	Light green.	Very light blue.
22	15	Fawn yellow.	Dull blue.	Fine grass green.	Grayish blue.
23	20	Deep fawn yellow.	Bluish gray.	Walnut-leaf green.	Whitish blue.
24	25	Chocolate brown.	Yellowish blue.	Reddish green.	White gray.
25	30	Red chocolate.	Yellowish green white.	Fine red.	Weak bluish white.
26	35	Purple lilac.	Very light greenish yel.	Fine deep blue.	Dull white.
27	40	Violet purple.	Dull white.	Same blue.	Dull white.
28	45	Indigo.	Light greenish yellow.	Same blue.	Yellowish white.
29	50	Lapis lazuli.	Greenish yellow.	Lightish blue.	Undecided yellow wh.
30	55	Prussian blue.	Yellow a little greenish.	Prussian blue.	Weak yellow.
31	60	Deep azure.	Fine yellow.	Same blue lighter.	Light yellow.

I chose rather to pass thus from one colour to another by a gradual transition than to proceed by abrupt intervals, which would have given me more decided results. In verification I have noted the colours of the two circles for the first sixty degrees of the second quadrant, although they were only the repetition of those which we had obtained in the first, with the sole difference of a change of their positions.

Allowance being made for the very great difficulty which is met with when a tint little different from another belonging to the same colour has to be specified, it will be seen by inspection of this table that D*** sees the blue, white and yellow as we do; but that he mistakes in the purple, lilac and brown, confounding them with red and blue.

Mr. Taylor and I noted the yellow and blue tints of the sixteenth observation as equal in brightness, and the daltonian made the same remark on the tints of the same name of the thirty-first reading, which is not distant from them 90°. It re-

sults that the appreciation of *the equality of intensity* of two complementary colours is not the same with him as with us,—a consequence which I had previously deduced from the experiments made with the coloured glasses numbered 6, 7, 13 and 18 (Table I.). The very great number of trials by which D*** was examined show, moreover, with extreme probability, that he does not perceive differences between colours which appear to us identical. M. Seebeck has come to the same conclusion*.

D*** assured us moreover that he found a total and abrupt difference between the colours of the twenty-fifth and twenty-sixth observations, circle right,—colours which pass at once from the finest red to very rich deep blue. To our eye the distinction was far from being so marked, which shows that his visual organ was unable to perceive the different mixtures of the red which accompany the blue to make it pass into purplish violet,—a red which becomes so evident when two or several plates of cobalt blue glass are superposed and are placed between the eye and an object in a good light. This precise circumscription of the constitutive domain of a colour is a fact which seems to me new and worthy of being remarked.

I shall notice, lastly, another striking observation. On the 10th of December, 1839, near 2 o'clock P.M., we were engaged in repeating the preceding experiments with the same apparatus similarly arranged. The sky was slightly overcast, and the indications of the daltonian corresponded exactly to those of which I have above given the abstract. Suddenly the sun shone out, and cast much more light upon the apparatus and the observer. The latter immediately told me that the colours assumed a different tint to his sight, and all reddened in a sensible manner. He called red that which he before named green and ill-defined blue. For myself, I could see no other change in the colours than an increase of their brilliancy and strength. I also consider it very probable that his impossibility of determining the shades of the plates marked 27, 1, 20, 35, 34, 3 and 4, proceeded from the obscurity of their tint. Perhaps he would have assigned to them a particular one if a brighter light than that of the sun had illuminated them, or if their thickness had given passage to a greater proportion of the rays of that luminary†.

* Mem. cited, p. 219.

† M. Seebeck thinks that when two colours are different, the eye of the daltonian may make him perceive that difference, but never greater than it appears to a normal eye.—(Mem. cit. p. 179, note.)

A problem which had not hitherto been attempted to be solved, is that of the difference which must exist between a daltonian and a person of normal vision in the perception of the complementary colours. In order to obtain some results on this point, I presented to D*** a sheet of paper on which were painted the colours of the spectrum with their complementary ones opposite. I give in Table III. by the side of their true names those which he assigned to them. This table proves clearly, and as might have been expected, that the colours which we regard as complementary do not appear such to the daltonian*.

TABLE III.

Experiments on Complementary Colours.

Names of the Natural Colours.	
According to me.	According to the daltonian.
1. Red.	Red (rose leaf).
2. Orange.	Reddish yellow.
3. Yellow.	Chrome yellow.
4. Green.	Weak green.
5. Blue.	Deep blue.
6. Indigo.	Blue (reddish tinted). ?
7. Violet.	Full blue.
8. Black (Indian).	Brown. ?
9. White.	White.
Names of the Complementary Colours.	
According to me.	According to the daltonian.
1. Greenish blue.	Light red (flower of the rose).
2. Blue.	Bright blue.
3. Indigo.	Indistinct blue.
4. Reddish violet.	Red. ?
5. Red orange.	Yellow. ?
6. Yellow orange.	Deeper yellow.
7. Greenish yellow.	Light yellow.
8. White.	White.
9. Black (Indian).	Brown. ?

D***'s eye is not however insensible to the *accidental colours*; but the fatigue which results in their production from the voluntary and sustained fixation of the illuminated object seems to be more painful to him than to us. The following are two of the experiments in which I succeeded best.

I placed a disc of rose-coloured paper $0^{m}{\cdot}05$ in diameter on

* M. Seebeck has found in various daltonians a very imperfect perception of the contrast of colours.—Mem. cit. p. 184.

a deep green sheep leather, and I exposed it to the intense light of the sun. After looking at it for some instants, D * * * having raised his eyes to the white ceiling, saw there a black circle surrounded with red. The colours had changed places instead of becoming complementary.

I then painted a human head, giving to each part a complementary colour. Thus the hair and the eyebrows were white, the flesh brownish, the sclerotica black, the lips and cheeks green, &c. When I asked him what he thought of the head, he replied that it appeared to him natural, that the hair was covered with a white cap little marked, and that the carnation of the cheeks was that of a person heated by a long walk.

It may further be interesting to remark, that D * * * sees, in the whole extent of the solar spectrum which is luminous to him, the black stripes of Fraunhofer exactly as an ordinary eye. This I have proved both by projecting these lines on a screen, and by showing them to him through a spy-glass, and making him place the vertical thread of a micrometer in coincidence with them. Daltonians therefore perceive darkness where it exists to us also.

*Second observation**.—H. Dickinson of Newcastle-upon-Tyne, a draper, has related in the following terms the peculiarities of his daltonism.

As far as I can systematize my experience, the primitive colours are red, yellow and blue: all the others are only different shades of these three types.

My standard red is the colour of sealing-wax. The leaves of the trees, a lively grass green, especially that of the laurel-leaf differs from it but extremely little.

I see yellow and blue in the ordinary manner, and I rarely confound objects which are tinted with them, although many things appear to me blue which do not appear so to others; a red cabbage is by day a magnificent bright blue, whilst I am surprised at finding it red by candle-light†.

If I look at a cherry-tree, the cherries on which are ripe, I distinguish them from the leaves only when I am near enough

* I owe the details of it to my friend Dr. Scholfield of Doncaster, who sent them to me dated August 17, 1841.

† M. M * * * of G. being pressed to paint by night the portrait of a person whose departure was fixed for the following morning, used yellow for rose-colour. She nevertheless kept the work of the celebrated painter, assuring him that she would only show it after sunset.

to know them by their form*. It will be seen that I have no perception of green, which to the majority of observers is the predominant colour in nature. It appears to me always red in daylight, and some of its varieties seem to me blue in artificial light.

This anomaly dates from my earliest childhood, and has been transmitted to me by several of my ancestors.

IV.

Examination of the Explanations of Daltonism.

Several opinions have been put forth, especially in England, to account for daltonism. I purpose to indicate them here in a succinct manner, accompanying them with some critical remarks on their value in the present state of our knowledge.

Mr. Dugald Stewart, after having noticed in his 'Philosophy of the Human Mind'† that there exist differences among men in the perception of colours, considers that the cause of it exists much more frequently in a weakness or in an error of conception than in a defect of the organ. This view of the subject accords with the hesitation which some daltonians have to name an isolated colour, although they have characterized it by comparison. There might also be urged in its favour that diversity which we have seen prevail between them when called upon to name the same colour‡. But it seems to me difficult to reconcile with this circumstance the fact that many individuals affected with daltonism have had a taste for painting, and that the one whose history I have sketched had not from his infancy the same incapacity for judging of colours. Moreover, the modest Scotch philosopher adds, that in giving this conjecture he is far from pretending that there may not be cases in which the affection is produced by the alteration of the eye. It may be that the sen-

* A daltonian in the same way painted a fir-tree in the midst of a landscape of a beautiful red.

† The first edition is that of 1792, the second that of 1802. See P. Prevost, *Essais de Philosophie*, tome i., p. 249. The illustrious philosopher of Edinburgh was insensible to the least refrangible colours of the spectrum, and could not distinguish a red fruit from the green leaves of the tree. (Chambers' Edinb. Journ. vol. iv. No. 171. Brewster's Treatise on Optics, p. 311.)

‡ Dr. Butter of Plymouth, also concluded from the examination of young Tucker, that daltonism has a physiological and not an optical cause, since all the other functions of the eye preserve their exercise entire. (Edinb. Phil. Journal, tome vi. p. 141.)

sation does not take place, or that the weakness of the impression may be such as to act as a cause of producing a habit of inattention, from which results the incapacity of conceiving the recollection of it. M. Prevost, who relates the explanation of Stewart, states that he does not adopt it*, but declares himself a partisan of that which I shall proceed to explain.

Dr. Dalton† concludes, from his personal observations, that the humours of his eyes and of those of his pupils are coloured blue‡. He admits that this coloration must be peculiar to the vitreous humour, for if it had affected another part of the organ it would have been discovered by an external inspection. In spite of the attempts of the author to explain by this theory the different facts of vision which he described, in spite of the reasonings of Prof. Prevost to obviate the objections (apparent according to him) which have been made thereto, it does not seem to me that it can be admitted. First, it could not explain the diversity of names given to the same colour by different daltonians: secondly, if the passage of the luminous rays through a blue medium sufficed to produce daltonism, the habitual use of blue glasses for spectacles would have long ago confirmed this hypothesis, against which it forms on the contrary a very strong argument. It is known that old men in whom the crystalline takes an amber tint, continue to see objects with their proper colours. Lastly, the most distinguished oculists and surgeons of Switzerland, Germany, England, France and the Low Countries, whose opinions I have been able to collect, are unanimous in not quoting any case of this blue coloration of the vitreous humour; and the best analytical works that we possess upon the mechanism and composition of the eye, the works of Thomas Young§, of Chenevix||, of Nicolas**, of Berzelius††, &c., all

* Dr. Elliotson likewise rejects this hypothesis. See Froriep's *Neue Notizen*, 1839, No. 247.

† Mem. of Manchester, vol. v. p. 30.

[‡ From a dissection of Dr. Dalton's eyes by Dr. Ransome of Manchester, it is now certain that the vitreous humour of both was not *blue* but *colourless*.—Ed.]

§ Thomas Young. On the Mechanism of the Eye, Phil. Trans. 1801, part 1, p. 33. *Bibl. Univ.*, tome xviii. p. 225.

|| R. Chenevix. On the Humours of the Eye, Journ. of the Roy. Institution. *Bibl. Brit.*, tome xxii. p. 345.

** Nicolas, Dr. and Prof. *Mémoire Analytique sur les différentes Humeurs de l'Œil, dans les vues de découvrir leur nature et les causes qui peuvent donner lieu à cette maladie désignée sous le nom de Cataracte. An. de Chim.*, tome liii. p. 307.

†† J. Berzelius. *Vues générales sur la composition des Fluides Animaux.* Medico-Chirurgical Transactions of London, t. iii. *Bibl. Brit.*, t. liv. p. 27.

tend to confirm this testimony. The opinion of Dalton cannot therefore be adopted.

On the contrary, Goethe* thinks that to explain daltonism it is sufficient to admit that those affected do not see blue, but in its place a weak purple, a rose-colour and a light and pure red. This led him to give the name of *Akyanoblepsis* to this affection. It is to be presumed that if he had known the different cases which I have described, he would not have advanced an hypothesis which suits so little with many of them.

All natural philosophers know that the limits of perceptible sounds vary between one ear and the other,—a fact which Wollaston and Chladni have incontrovertibly demonstrated. Sir D. Brewster† supposes, by analogy, that in the cases of daltonism the eye is not impressed by the colours of one of the extremities of the spectrum. "The insensibility of some eyes to weak impressions of light, requires," says he, "no other explanation, than that either from original organisation, or some accidental cause, the retina of one person may be less delicate and less susceptible of luminous impressions than the retina of another, without being accompanied with any diminution of the powers of vision." But the more recent researches of M. Savart having established the fact that in suitable circumstances the limit of the sounds perceived by the same ears may be considerably modified and extended, and nothing similar having been able to be proved in what concerns the defect, the cause of which we are investigating, it appears to me that this theory wants proofs‡. It is known, moreover, that the sensibility of the sound eye is comparatively much less than that of the ear, for if we represent the length of undulation in the air for the extreme red by $0^{pc}{\cdot}0000266$ (English measure), and for the extreme violet by $0^{pc}{\cdot}0000167$, we see that the relation of the corresponding vibrations is that of 1·59 to 1, a value a little below 1·6, which is that of the minor sixth, and consequently much lower than that of an octave.

At a later period the illustrious natural philosopher of St. Andrews appears to have changed his opinion§; setting out

* Goethe. *Zur Farbenlehre*, §§ 111 to 113. Wh. Nicholl also (Annals of Philosophy, No. 8, tome iii.) attributes it to the absence of sensibility for blue.

† Mackenzie, *op. cit.* Edinb. Journal, vol. vi. p. 141. [See Sir David Brewster's remarks on this paragraph in the Philosophical Magazine for August 1844, p. 134.—Edit.]

‡ See Sir D. Brewster in Phil. Mag., *ubi supra.*

§ Edinb. Journ. of Science, tome vii. p. 86. [See Sir D. Brewster's reply in the Philosophical Magazine for Aug. 1844, p. 137.]

from the supposition that the choroïd is essential to vision, he conjectures that the invisibility of the red colour to daltonians is owing to the retina itself having a blue tint, so that the light being deprived of its red rays by the absorbent power of that membrane, the coloured impression upon the choroïd will be destitute of red. The same objections drawn from anatomical data, and from the influence of the glasses upon the perception of colours, would suffice to overthrow this hypothesis, if it were not contradicted by facts. We have seen that D*** and others were able to appreciate red in the spectrum.

According to the phrenologists, the distinction of colours is a faculty which does not depend upon the eye, but on a particular part of the brain, which they term the *organ of colours*. "Observation proves," says Mr. Combe*, "that those individuals in whom the portion of the brain which is immediately above the eye, beneath the eyebrow, is largely developed, possess in a high degree the faculty of distinguishing colours." It is thus the imperfection of this organ which is the origin of daltonism, and the proof is that those who are affected with it possess an ocular apparatus whose mechanical construction and optical effects are faultless.

The *Gazette des Hôpitaux* of October 19, 1839, remarks that the first period of amaurosis is accompanied with a confusion of colours which, like the natural achromatopsy, appears to depend on a diseased state of the brain. In a *gutta serena* arising from hypererethysm, the least vivid colours, such as blue and violet, are perceived in the most distinct manner, and yellow objects appear red; whilst if the malady is produced by weakness, the red light in the end disappears, and does not become visible again till the cessation of the morbid state.

Professor Muncke endeavours to explain the phænomena of which we are treating by the following hypothesis†. Let us suppose that in what concerns the activity of the optic nerve there are only two colours with their complementary ones, the blue and red with the yellow and green; the first characterized by its chemical power, the second by its calorific power; all the other colours will be deduced from mixtures and shades of these

* System of Phrenology. I must say that among the daltonians whom I have examined, the organ in question was in general but little evident, except in two of them, in whom it was remarkably prominent.

† Gehler's *Physikalisches Wörterbuch*, 2^tm Aufg., tome iv. p. 1428; art. *Gesicht*. (Leipsig, 1828.)

four, in what relates to their physiological influence upon the eye. It is consequently sufficient to admit that the nerves are more or less sensible to the heating action of light, in order to understand that in all possible cases the yellow, which is the most luminous colour, will be recognised entirely and exactly, whilst all the other colours will only be apparent by opposition; this is the reason why green and red are not distinguished, and are often confounded with blue and yellow. We know, by a multitude of experiments, that the eye is the least sensible to red and green*.

Lastly, Sir J. W. Herschel† and Dr. Elliotson‡ are of opinion that this malady of the vision must be attributed to a defect in the sensorium itself, which renders it incapable of appreciating exactly the differences which exist between the rays, and on which their particular colours depend. This view is evidently only a formula of facts; it is the only one against which no objection lies. It has been adopted both by Mr. Harvey§ to account for cases which he has described, and by Dr. Young, who, setting out from the observations of Darwin, admits the absence or the paralysis of the fibres of the retina designed for the perception of red‖.

Whatever, in conclusion, are the circumstances which have engendered or which characterize this remarkable affection, it is of the number of those which the Esculapian art is unable to destroy. The most celebrated oculists, such as the Mackenzies¶, Jüngkens**, Maunoirs††, &c., are unanimous on this point.

There nevertheless exists a very easy means of rectifying, to a certain extent, the error of the appellation of colour. This means consists in examining coloured objects through a transparent medium, as a glass or a liquid, of a certain known tint. Suppose this tint red; the impression of a green body and of a red body,

* [This is not the case. When the sensibility of the eye is diminished, *red* is the first colour that disappears, and the *green* is left.—Ed.]

† J. W. Herschel. *Op. cit.* p. 434, § 507.

‡ Froriep's *Neue Notizen*, No. 247, 1839.

§ Harvey. Edinb. Phil. Trans., vol. x. p. 253. Edinb. Journ. of Science, vol. v. p. 114. *Bibl. Univ.*, tome xxxv. p. 84.

‖ Phil. Trans., vol. lxxvi. p. 344.

¶ Mackenzie. *Op. cit.*

** J. C. Jüngken, M.C., Dr. und Prof. der Heilkunde. *Die Lehre von den Augenkrankheiten, ein Handbuch zum Gebrauche bei Vorlesungen und zum Selbstunterrichte für angehende Aertze.* Berlin, 1832, 8vo. p. 841. ss.

†† Verbal communication.

the same at first to the naked eye, will become manifestly distinguished by the use of the transparent screen. This method appears to have been practised for the first time by Prof. Seebeck, the father, towards the year 1817*. Nothing can equal the surprise of a daltonian when the errors which he commits every day in the appreciation of colours are thus disclosed to him. Unhappily the tint of the coloured glasses and their number cannot be prescribed in advance; the impossibility of a rigorous classification of the innumerable varieties of daltonism obliges us to choose them *à posteriori* for each particular case. We may add, that their employment only remedies mistakes in the specific nature of colours, and leaves in general those which apply to the shades of one and the same tint.

V.

Recapitulation.

In recapitulation, I have sought to establish the following facts:—

1. That daltonism was not investigated by the ancients.
2. That among the moderns it has only been authentically proved in individuals of the white race.
3. That there exists a very considerable number of varieties of it, from those persons who only perceive two colours, or rather two sensations,—the one of brightness, the other of obscurity,—to those who even by candle-light confound only colours which closely approximate, such as shades of blue and green of equal intensity.
4. That there are many more daltonians than is generally supposed.
5. That the female sex furnishes a very small proportion.
6. That they can, in certain cases, be recognised by some external signs.
7. That there are as many with blue as with black eyes.
8. That daltonism is not always hereditary.
9. That it does not always affect all the male members of the same family.
10. That it does not always date from the birth.
11. That daltonians do not judge of complementary colours as we do.

* Seebeck. Mem. cit. p. 216.

12. That several of them are not sensible to the least refrangible rays.

13. That they see, as we do, the lines in the spectrum discovered by Fraunhofer, consequently the limits of brightness and of interior obscurity of the spectrum.

14. That they do not judge as we do of the contrast of colours.

15. That their affection does not proceed from a vicious conformation of the eye, nor from any coloration of the humours of the retina.

16. That the state of daltonism may be altered by means easily employed.

17. That it has its origin in a defect of the sensorium.

SCIENTIFIC MEMOIRS.

VOL. IV.—PART XIV.

ARTICLE VII.

On the Heat and Elasticity of Gases and Vapours. By C. HOLTZMANN, *Professor of Natural Philosophy and Mathematics at the Lyceum, Manheim* *.

[From a Pamphlet published in a separate form. Manheim, 1845.]

PREFACE.

POISSON has published a treatise † upon the dependency of the density and elasticity of a gas on the quantity of heat it contains, which is based on the correctness of Mariotte's law, of Gay-Lussac's law of the constancy of the coefficient of expansion on the application of heat, on the assumption that the relation of specific heats, when the pressure and the volume are constant, is independent of temperature and pressure; and, finally, on the supposition that the quantity of heat increases in proportion to the expansion of the air, the pressure being constant.

Of these assumptions the two first are undoubtedly firmly established, at least within very wide limits; but the third, respecting the relation of the specific heats, is certainly incorrect, as is evident from Clapeyron's treatise on the motive power of heat ‡, and as will equally appear from this treatise.

It is from this cause that the results of Poisson's investigation are not in harmony with experience, which is most di-

* From the German by W. Francis, Ph.D., F.L.S.

† *Ann. de Chim. et Phys.* xxiii. 337, or Gibbert, *Ann.*, lxxvi. 269; likewise Poisson, *Traité de Mécanique*, 2 ed. ii. 637.

‡ *Journal de l'Ecole Polytechnique*, t. xiv. 170, and also Scientific Memoirs, vol. i. part 3, p. 347.

stinctly evidenced, and was even recognised by Poisson himself, when they are applied to vapours.

A second treatise on this subject is the one just mentioned by Clapeyron, in so far as it relates to gases. It is founded on a work by S. Carnot, which I have not been able to procure, and sets out from the view, which is certainly correct, that *in the passage of heat from one body to another the mechanical action developed by the transferer of the heat is independent of the nature and extent of this bearer* *.

The results he has obtained are correct, so far as the laws of Mariotte and Gay-Lussac, assumed by him, are valid; but his formulæ contain an undetermined function, which in the more direct way I have taken is determined, and which gives to those formulæ applicability and their true import.

I first show how the effect of the heat added to a gas may be represented by a purely mechanical action, *i. e.* by a weight which is raised a certain height; this effect I assume as the arbitrary measure of the heat, and I arrive by this means at an expression for the quantity of heat contained in a quantity of gas at a given pressure and at a given temperature, and this without the employment of any hypothesis.

One function remains undetermined in this expression; I assume, in order to determine it, that the specific heat of a gas is independent of the temperature, and I adduce the facts which render this assumption most highly probable. With this then the quantity of heat in the given gas is fully determined.

Applications are then made of this determination to those phænomena which are exhibited in variations of the density and of the temperature of the atmosphere, and the statements arrived at by theory compared with those of experiment, if any such exist.

With the assistance of the proposition recently confirmed by De Pambour, that the quantity of heat is constant in vapours at the maximum of tension, the expression advanced gives a formula for the quantity of heat which indicates the elasticity of the vapour by its temperature; this is the same formula to which Roche and Von Wrede arrived with other coefficients, and in accordance with which Magnus combined the results of his observations.

From this formula then I determine the expansion of vapours

* Poggendorff's *Annalen*, vol. lix. p. 462.

by heat, when a beautiful confirmation results with respect to steam, for the densities of the aqueous vapours with the proper coefficient of expansion turn out exactly as Gay-Lussac, Schmeddingk and Munke found them, for different temperatures.

The formula given, moreover, serves to determine the specific heats of vapours, respecting which we had previously scarcely any information.

At the conclusion I give some other formulæ for calculating the effect of steam-engines founded on the preceding, and I show how great an amount of the motive force of the heat in steam-engines is lost from its being everywhere requisite to overcome the cohesion of the water in the formation of steam. The formulæ here given are purely theoretical; but they are the fundamental basis of a practical theory of the steam-engine corresponding to the present state of science.

Manheim, Aug. 1844. C. HOLTZMANN.

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§ 1. *Determination of the Quantity of Heat.*

If heat be added to a quantity of gas which I imagine to be in a vessel impermeable to heat, the phænomena resulting are, increase of temperature, of elasticity and of volume; and there may occur,—

a. Increase of temperature and of elasticity without any change in the volume; and

b. Increase of temperature with change of volume, but without any alteration of the elasticity.

In the first case no motion of matter occurs; in the second case, on the contrary, the effect of the heat is in part increase of temperature and in part a motion of matter. But the effect of the heat may likewise be simply represented by a generated motion. For this purpose it is only requisite in both the cases considered to allow the gas to expand without alteration of its quantity of heat, until it has again acquired the previous temperature. In this case the effect of the heat added consists solely in this expansion, and consequently the pressure under which the gas stands is driven back through a certain space, which in all cases must be regarded as equivalent to the raising of a weight to a height, so that in this case the effect of the heat consists solely in a mechanical action, and is measured by it.

The effect of the heat added to the gas is consequently either increase of temperature combined with increase of elasticity, or a mechanical action, or a combination of the two; and a mechanical action is the equivalent of the increase of temperature.

2. Heat can only be measured by its effects; of the two effects mentioned the mechanical action is especially adapted for this purpose, and will be employed in the following pages.

I term *unit of heat the heat which on its addition to any gas is capable of producing the mechanical action* a, *i. e.* to use a definite measure, which can raise *a* kilogrammes 1 metre.

3. To render it more intelligible, I now imagine any gas in a vertical cylinder of 1^{mq}* section, which is impermeable by heat, closed above by a moveable piston. This piston must be pressed down by a weight p kilogrammes, equal to the pressure of the gas, if the gas is to maintain its volume. Let the infinitely small quantity of heat dq be added to this gas, and by diminishing the pressure let the gas expand until it has again acquired the former temperature. Let this expansion be dv; it is attained by the gas forcing up the piston, and the pressure resting on it, dv in height. The effect of the heat dq is consequently the mechanical action $(p-dp)$ kilogrammes raised to dv metres, or $(p-dp).dv$ kilogrammes to 1 metre.

dp expresses the necessary diminution of the pressure; it is infinitely small, and therefore disappears in comparison to p. The mechanical action of the heat dq is then $p.dv$, and the action of the unit of heat,

$$\frac{p.dv}{dq},$$

which according to No. 2 is equal to a.

If ϱ be the density of the gas, *i. e.* the weight of the unit of volume, the volume of m kil. gas is

$$v=\frac{m}{\varrho}$$

and

$$dv=-\frac{m.d\varrho}{\varrho^2},$$

therefore the above equation

$$-\frac{mp.d\varrho}{\varrho^2.dq}=a. \quad \ldots\ldots\ldots \quad (1.)$$

4. The quantity of heat q in 1 kil. gas depends on the pressure p to which the gas is subjected, the density ϱ and the tem-

* 1^{mq} denoting one square metre.

perature t of the gas. These three magnitudes are related by the known equation (Mariotte's and Gay-Lussac's law),

$$p = k\varrho(1+\alpha t), \quad \ldots \quad (2.)$$

in which k is a separate coefficient for each gas, and α the coefficient of expansion of the gas on the application of heat; q may therefore be simply considered as a function of p and ϱ. Its complete differential is then

$$dq = \frac{dq}{dp} \cdot dp + \frac{dq}{d\varrho} \cdot d\varrho,$$

on which account the above dp and $d\varrho$ depend in such a manner on one another that the temperature remains constant. The equation (2.) however gives for this case

$$dp = k(1+\alpha t) \cdot d\varrho = \frac{p}{\varrho} \cdot d\varrho,$$

and consequently $$dq = \left(\frac{p}{\varrho} \cdot \frac{dq}{dp} + \frac{dq}{d\varrho}\right) \cdot d\varrho.$$

Above, the increase of the quantity of heat refers to m kil. gas, but in this case q relates to the unit of the weight; if the latter relation be retained, then $m \cdot dq$ should be substituted above for dq, and the equation (1.) now becomes

$$-\frac{p}{p\varrho \cdot \frac{dq}{dp} + \varrho^2 \cdot \frac{dq}{d\varrho}} = a,$$

or

$$p \cdot \frac{dq}{dp} + \varrho \cdot \frac{dq}{d\varrho} = -\frac{p}{a\varrho}.$$

The general integral of this partial differential equation is

$$q = \mathrm{F} - \mathrm{NL}^{*} p \cdot \frac{p}{a\varrho},$$

where F denotes any function of $\frac{p}{\varrho}$. But since $\frac{p}{\varrho} = k(1+\alpha t)$, we can likewise substitute for this function a function of t, which from its arbitrary nature may also be expressed by

$$\mathrm{F}_t + k\frac{(1+\alpha t)}{a} \cdot \mathrm{NL}\, p_0,$$

in which p_0 is intended to express any constant pressure. Consequently

$$q = \mathrm{F}_t - k\frac{(1+\alpha t)}{a} \cdot \mathrm{NL}\frac{p}{p_0}. \quad \ldots \quad \mathrm{I.}$$

* Denoting the Napierian logarithm of p.

5. The *specific heat* is the quantity of heat which must be added to the gas to raise the temperature 1°. If the addition of the quantity of heat dq increase the temperature by dt, the quantity of heat $\frac{dq}{dt}$ would be required to increase the temperature 1°. Or the relation between q and t gives the specific heat of the gas, viz. the specific heat under a constant pressure when is considered constant, and the specific heat under a constant volume when ϱ is considered constant.

Let c denote the specific heat with constant pressure, and

c_1 ... ... volume,

we have

$$\left.\begin{aligned} c &= \frac{dq}{dt} = \frac{dF}{dt} - \frac{k\alpha}{a} \cdot \text{NL}\frac{p}{p_0} \\ c_1 &= \frac{dq}{dt} + \frac{dq}{dp} \cdot \frac{dp}{dt} = \frac{dF}{dt} - \frac{k\alpha}{a} \cdot \text{NL}\frac{p}{p_0} - \frac{k\alpha}{a} \end{aligned}\right\} \text{II.}$$

In this the unit of weight is the basis; if it be desired to refer the specific heats to the volume, we have to multiply by the specific gravities, or by $\varrho = \frac{p}{k(1+\alpha t)}$. This affords

$$\left.\begin{aligned} c' &= \frac{p}{k(1+\alpha t)} \cdot \frac{dF}{dt} - \frac{p\alpha}{a(1+\alpha t)} \cdot \text{NL}\frac{p}{p_0} \text{ and} \\ c'_1 &= \frac{p}{k(1+\alpha t)} \cdot \frac{dF}{dt} - \frac{p\alpha}{a(1+\alpha t)} \cdot \text{NL}\frac{p}{p_0} - \frac{p\alpha}{a(1+\alpha t)} \end{aligned}\right\} \text{III.}$$

6. There now remains to determine the function F_t. From the experiments of Dulong on the value of the relation of the two specific heats, it follows that this relation is independent of the temperature. He has deduced these values, as is well known, from the tones which a pipe gives filled with various gases. He mentions an experiment in which a pipe that gave a tone at 22° C., which results from 500 vibrations in the second, produced at 4° C. only 484·8 vibrations. If the relation of the specific heats remains in this interval the same, the numbers of vibrations are as

$$\sqrt{1+0{\cdot}003665 \cdot 22} : \sqrt{1+0{\cdot}003665 \cdot 4},$$

whence, if we start from the first tone, we obtain the number of vibrations 484·5 for the second. The coincidence of the calculated and of the observed value is so great that a change in the relation of the two specific heats by increase of temperature must at least be very small.

If this relation is independent of the temperature, there results simply $\frac{dF}{dt}$ constant and

$$F_t = A + bt,$$

in which A and b are constants.

Moreover, the direct experiments of Gay-Lussac and Welter are in favour of this assumption, who found the relation under consideration independent of the temperature or pressure; and also the coincidence of the values of the specific heats ascertained by De la Roche and Bérard with those of other observers, notwithstanding that they submitted the gases in the experiment to 100° C., while in the observations of others the gases had only a temperature of 10° to 20°.

The experiments of Dulong and Petit on the refrigeration by gases, likewise show that the specific heat of gases is independent of the temperature; these philosophers found that the cooling varies, indeed, with the pressure, but not with the temperature of the gases.

From all this it results that we are justified, in the present state of science, in substituting $A + bt$ for the function F_t, at least as a very close approximation.

7. The formulæ of the preceding paragraphs now become

$$\left.\begin{aligned} q &= A + bt - \frac{k(1+\alpha t)}{a} \cdot \text{NL}\frac{p}{p_0}, \\ c &= b - \frac{k\alpha}{a} \cdot \text{NL}\frac{p}{p_0}, \\ c_1 &= b - \frac{k\alpha}{a} \cdot \text{NL}\frac{p}{p_0} - \frac{k\alpha}{a}. \end{aligned}\right\} \quad \text{IV.}$$

8. We have still to determine the arbitrary quantity a. This being arbitrary, the unit of heat (2.) dependent on it may itself be selected at will, and a, conversely, be determined by it. I therefore take, as is usually done, the quantity of heat which is capable of heating 1 kil. water at 0° to 1° as unit of heat.

According to the determination of De la Roche and Bérard, the specific heat of the atmospheric air, with a pressure of one atmosphere, is equal to 0·267 of the unit of heat just established. If we take p_0 = to the pressure of an atmosphere, we obtain $\text{NL} \cdot \frac{p}{p_0} = 0$, and therefore for atmospheric air $c = b = 0{\cdot}267$.

In the same manner $\frac{c}{c_1}$ is for atmospheric air, calculated from the velocity of sound, $= 1{\cdot}415$, also under the pressure of one atmosphere. Consequently $0{\cdot}267 = 1{\cdot}415\ c_1$ and $c_1 = 0{\cdot}189$, whence $c - c_1$, that is, there results, according to (IV.), $\frac{k\alpha}{a} = 0{\cdot}078$.

But k is $= \frac{p}{\varrho(1+\alpha t)}$.

At the same time p is the pressure on 1^{mq} and ϱ the weight of 1^{mc}* atmospheric air under that pressure and at the temperature t^0. Now we have for the pressure of one atmosphere $p = 10333$ kil., and for the temperature of the freezing-point $\varrho = 1{\cdot}299$ kil. Consequently

$$k = \frac{10333}{1{\cdot}299} = 7955;$$

α is, according to Magnus, equal to $0{\cdot}003668$. With these numbers we obtain

$$a = \frac{7955 \times 0{\cdot}003668}{0{\cdot}078} = 374.$$

This result indicates that the heat which warms 1 kil. water 1° C. is capable of raising 374 kilogrammes 1 metre. Clapeyron obtained the same result, but gives it in more complicated numbers.

I will now attempt to determine how far this value of a is trustworthy. The extreme values which were obtained for b are, according to De la Roche and Bérard, $0{\cdot}290$ and $0{\cdot}250$, and the results of other experimenters likewise fall within these limits. Gay-Lussac and Welter found for the relation $\frac{c}{c_1}$ the value $1{\cdot}372$, which we may regard as the lowest limit of the probable values for this relation. By combination of these numbers we obtain as the smallest value $a = 343$, and as the highest value 429, whence it results that 374 is, it is true, a mean value, but may possibly be erroneous about 40.

§ 2. *Heat and Elasticity of Gases.*

9. If a gas be brought from the pressure p under the pressure p' without heat escaping, the temperature and density are altered. These changes may now be calculated from the formulæ

$$q = A + bt - \frac{k(1+\alpha t)}{a} \cdot \text{NL}\frac{p}{p_0},$$

* Denoting one metre cube.

$$q = A + b\,t - \frac{k\,(1 + \alpha\,t')}{a} \cdot \text{NL}\,\frac{p'}{p_0},$$

and thence

$$t' - t = \frac{\dfrac{k\,(1 + \alpha\,t)}{a} \cdot \text{NL}\,\dfrac{p'}{p}}{b - \dfrac{k\,\alpha}{a} \cdot \text{NL}\,\dfrac{p'}{p_0}}. \quad \ldots\ldots\ldots \quad (1.)$$

This formula gives the increase of temperature which originates from the compression. The density of the gas may then be calculated from the formula

$$\varrho' = \frac{p'}{k\,(1 + \alpha\,t')};$$

the degree of the condensation is obtained from

$$\frac{\varrho'}{\varrho} = \frac{p'\,(1 + \alpha\,t)}{p\,(1 + \alpha\,t')}. \quad \ldots\ldots\ldots\ldots \quad (2.)$$

We have for atmospheric air, when p_0 is made equal to the pressure of one atmosphere,

$$b = 0{\cdot}267\,; \quad k = 7955\,; \quad \alpha = 0{\cdot}003668\,; \quad a = 374.$$

On substituting these values in the equation (1.), and at the same time substituting Briggs's logarithms for those of Napier, we obtain

$$t' - t = \frac{0{\cdot}180\,(272{\cdot}7 + t) \cdot \log \dfrac{p'}{p}}{0{\cdot}267 - 0{\cdot}180 \cdot \log \dfrac{p'}{p_0}}. \quad \ldots\ldots\ldots \quad (3.)$$

For $t = 0°$ and $p = p_0 = 1$, we obtain, according to these formulæ, for the pressures of 2, 3, 4, 5 and 10 atmospheres, the following increase of temperatures and condensations:

$p' =$	$2p$,	$3p$,	$4p$,	$5p$,	$10p$.
$t' =$	$69°{\cdot}4$,	$129°$,	$186°$,	$243°$,	$563°$.
$\frac{\varrho'}{\varrho} =$	$1{\cdot}59$,	$2{\cdot}04$,	$2{\cdot}38$,	$2{\cdot}64$,	$3{\cdot}26$.

The increase of the temperatures is greater than results from the formula given by Poisson. There exist on this subject no experiments which are in any degree trustworthy.

10. When air is compressed and then allowed to cool until it has again assumed its former temperature, the quantity of heat $q - q'$ given off is equal to

$$\frac{k\,(1 + \alpha\,t)}{a} \cdot \text{NL}\,\frac{p'}{p}, \quad \ldots\ldots\ldots \quad (4.)$$

when p is the original and p' is the subsequent pressure. Since in this case Mariotte's law obtains, we can also write for $\frac{p'}{p}$ the relation of the densities $\frac{\varrho'}{\varrho}$.

With the introduction of Briggs's logarithms the amount of heat given off for atmospheric air is

$$0{\cdot}180\,(273 + t)\,.\,\log\frac{p'}{p}.$$

At the temperature 0° the quantities of heat given off are,

	14·78,	23·42,	29·56,	34·32,	49·1,
for $\frac{p'}{p}$ equal	2,	3,	4,	5,	10.

With an equally great rarefaction the same quantities of heat are absorbed. Moreover, as will be seen from the formula, the quantity of heat given off with the same compression increases with the temperature at which the gas expands.

11. The above expression (4.) refers to the unit of weight; if it be desired to calculate the quantity of heat which is given off by the unit of volume at the pressure p, it is requisite to multiply by the density of the gas at this pressure, *i. e.* by $\varrho=\frac{p}{k\,(1+\alpha t)}$. In this manner the quantity of heat given off in the compression of one volume is found to be equal to

$$\frac{p}{a}\,.\,\mathrm{NL}\,\frac{p'}{p}.$$

Consequently for equal primitive pressure, equal volumes of all gases, the condensation being the same, give off equal quantities of heat.

Already Dulong advanced the same proposition, founded on his experiments and those of De la Roche and Bérard on the specific heats of gases; it likewise occurs in Clapeyron.

12. From the formulæ III. in No. 5, it is evident that the difference of the two specific heats referred to the unit of volume equals

$$\frac{p\,\alpha}{a\,(1+\alpha t)}.$$

For different gases, taken at the same pressure and the same temperature, this difference varies only with the coefficient of expansion α, and, since this is almost equal for the various gases, is itself nearly equal for all gases. Dulong has assumed this equality, and has calculated with it and the observed values of

$\frac{c}{c_1}$ the specific heats c and c_1 for the various gases, and has shown, *à posteriori*, the admissibility of that assumption from the coincidence of the values of c calculated by him with those observed by De la Roche and Bérard.

13. The specific heats of the gases are given above by the equations (IV.) No. 7. For atmospheric air we find

$$c = 0{\cdot}267 - 0{\cdot}180 \,.\log\frac{p}{p_0},$$

$$c_1 = 0{\cdot}189 - 0{\cdot}180 \,.\log\frac{p}{p_0}, \quad \ldots\ldots \quad (5.)$$

where c and c_1 are the specific heats, the pressure and volume being constant.

Only c can be measured directly; Suermann has published some experiments on the subject, which however by no means agree with this formula. We obtain, for instance, for $p_0 = 760$, and

	According to the formula.	According to Suermann.
$p = 691{\cdot}10$	$c = 0{\cdot}2744$	$0{\cdot}2866$
$p = 508{\cdot}86$	$c = 0{\cdot}2983$	$0{\cdot}2964$
$p = 319{\cdot}63$	$c = 0{\cdot}3347$	$0{\cdot}3149$

The values calculated from the formula follow, it is true, in general the same course as those observed, but they evidently increase at a greater rate. However, the observer himself has raised great doubt with respect to the admissibility of the observed values, to which indeed others might be added. This non-coincidence therefore must certainly not be regarded as a proof against the correctness of the advanced formula.

There are two experiments of De la Roche and Bérard which may be mentioned here; according to these, the specific heat of $1^{\text{lit.}}$ air measured at 0° and under the pressure $1^{\text{m}}{\cdot}0058$, and the specific heat of $1^{\text{lit.}}$ measured at 0° and under the pressure $0^{\text{m}}{\cdot}7405$, being in the ratio of 1·2044 : 1, or as 1·2396 : 1; the observers regard the latter number as far more accurate than the first.

According to the above formula, the specific heats of the units of weight with the pressures $1^{\text{m}}{\cdot}0058$ and $0^{\text{m}}{\cdot}7405$ equal 0·245 and 0·269: consequently the relation of these heats referred to quantities whose weights are in the proportion $\frac{1{\cdot}0058}{0{\cdot}7405}$ equal

$$\frac{1{\cdot}0058 \times 0{\cdot}245}{0{\cdot}7405 \times 0{\cdot}269} = 1{\cdot}237,$$

which agrees more accurately with 1·2396 than could have been expected in such observations.

14. The specific heat with constant volume is for atmospheric air

$$c_1 = 0{\cdot}189 - 0{\cdot}180 \,.\, \log \frac{p}{p_0}.$$

This formula would give for a pressure of somewhat more than 10 atmospheres $c_1 = 0$, which cannot be the case; for then the smallest quantity of heat added would certainly produce expansion, and an addition of heat with the retention of the volume would no longer be possible with this pressure. It is thence evident, that with respect to atmospheric air, the assumptions made, viz. that the coefficient of expansion α is constant, and that the specific heat is independent of the temperature, even with the pressure of ten atmospheres, cause a great difference between the results deduced from the formulæ here given and what actually obtains.

§ 3. *Specific Heat and Elasticity of Steam.*

15. The view that steam in the maximum of its force of expansion contains a quantity of heat not dependent on this force, and consequently likewise on the temperature, has been confirmed by the recent experiments of De Pambour. Therefore, if q represent this quantity of heat, p the force of expansion, and t the temperature of the steam, we have, according to No. 7,

$$q = A + b\,t - \frac{k(1+\alpha t)}{a} \,.\, \mathrm{NL}\frac{p}{p_0}.$$

Now, if we write for $p = p_0$ $t = 0$, that is, if we reckon the temperatures from that point at which the force of expansion of the vapours equals p_0, or, according to what precedes, equal to one atmosphere, consequently from the boiling-point, we have $q = A$, which, subtracted from the last equation, gives

$$0 = b\,t - \frac{k(1+\alpha t)}{a} \,.\, \mathrm{NL}\frac{p}{p_0},$$

or

$$\mathrm{NL}\frac{p}{p_0} = \frac{a\,b\,t}{k(1+\alpha t)} = \frac{a\,b}{k\,\alpha} \,.\, \frac{t}{\frac{1}{\alpha} + t} \quad . \quad . \quad . \quad (1.)$$

This equation gives the forces of expansion of the vapours of water for the temperature t, reckoned from the boiling-point.

If we introduce Briggs's logarithms, if we express the force of expansion in atmospheres, and write $M \,.\, \frac{a\,b}{k\,\alpha} = B$, in which M is the modulus of the Briggs's logarithm, we obtain

$$\log \frac{p}{p_0} = \frac{B\,t}{\frac{1}{\alpha} + t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

In this equation the two constants B and $\frac{1}{\alpha}$ are to be deduced from observations.

16. From some of the experiments of Magnus there accordingly results

$$\log \frac{p}{p_0} = \frac{5{\cdot}2555 \,.\, t}{336{\cdot}22 + t}. \quad \ldots \ldots \quad (3.)$$

The following table shows how far the values calculated according to this formula coincide with those observed by Magnus, and then gives a comparison of the results of this formula with those which Arago and Dulong obtained from their experiments:—

p.	t.		
In Millimetres.	Calculated.	According to Magnus.	Difference.
9·43	−89·49	−88·66	+0·83
9·88	−88·79	−88·02	+0·77
22·24	−75·95	−76·15	−0·20
71·20	−55·03	−55·10	−0·07
73·74	−54·34	−54·30	+0·04
114·65	−45·45	−45·26	+0·19
284·97	−25·20	−25·17	+0·03
387·15	−17·72	−17·75	−0·03
542·54	− 9·09	− 9·20	−0·11
563·50	− 8·09	− 8·19	−0·10

p.	t.		
In Atmospheres.	Calculated.	According to Arago and Dulong.	Difference.
2·14	+22·56	22·42	−0·14
2·8705	32·09	31·77	−0·32
4·5735	48·31	48·37	+0·06
6·4977	61·51	61·30	−0·21
7·3755	66·50	66·54	+0·04
11·632	85·52	85·78	+0·26
17·185	103·3	103·2	−0·1
17·285	103·6	103·9	+0·3
18·504	106·8	107·2	+0·4
21·555	114·3	114·7	+0·4
23·934	119·6	120·1	+0·5

The temperatures enumerated as observed in the experiments of Arago and Dulong are corrected for the air thermometer from the indications of the smaller thermometer exposed to the steam, according to the formula given by August*.

For the freezing-point, therefore, $t = -100°$, the formula

* Poggendorff's *Annalen*, xxii. p. 119.

gives the force of expansion = 4·529 millimetres. This is the mean of seven experiments by Magnus, and of sixteen experiments of the tenth series by Regnault; this number is one of the bases on which the calculation of the coefficients is founded.

The greatest deviations of the formula from the results of experiments are 0·83 and 0·77 degree of temperature, and it might be thought that this is too much, but in this case 0°·8 correspond to a difference of only 0·5 millimetre pressure; and even the formula advanced by Magnus, which was advanced with reference to these two observations (I have only made use of the eight others), differs as much in this instance from the result of experiment.

With the exception of these two differences all the others are very small, and come wholly within the limits of errors of observation, which includes even the highest pressure observed by Arago and Dulong, proving both the accuracy of Magnus's experiments and the correctness of the formula above advanced, and the theory on which it is founded.

The formula here obtained for the expansive force of vapours is moreover the identical one to which formerly Roche and subsequently Von Wrede arrived, but in different ways, in which the import of the coefficient B, to which I shall subsequently return, was not perceived by them*.

If it be desired to commence reckoning the temperature from 0° C., and to indicate the pressures in millimetres of the height of mercury, we may first substitute in the formula (3.) $t_1 - 100$ for t: this gives

$$\log \frac{p}{760} = \frac{5{\cdot}2555 \,.\, t_1 - 525{\cdot}55}{236{\cdot}22 + t_1};$$

consequently we have then in formula (3.) for $t = -100$, $p = 4{\cdot}529$,

$$\log \frac{4{\cdot}529}{760} = \frac{-525{\cdot}55}{236{\cdot}22}.$$

If we subtract these two equations from each other,

$$\log \frac{p}{4{\cdot}529} = \frac{\left\{5{\cdot}2555 + \frac{525{\cdot}55}{236{\cdot}22}\right\} . t_1}{236{\cdot}22 + t_1},$$

or

$$\log p = 0{\cdot}65600 + \frac{7{\cdot}4804 \,.\, t_1}{236{\cdot}22 + t_1},$$

* I am not acquainted with Roche's treatise, this, therefore, is merely supposition with reference to him.

instead of which we may also write

$$\frac{7{\cdot}4804\,.\,t_1}{236{\cdot}22 + t_1}$$

$$p = 4{\cdot}529{\cdot}10.$$

This formula differs but very little, by somewhat different coefficients, from that of Magnus. I might also have set out from this formula.

17. From the formula advanced, we find the coefficient of expansion of steam $= \frac{1}{336{\cdot}22}$ referred to the volume at boiling-point.

If it be desired to refer the expansion of steam to the volume at 0°, we find this for each degree of heat equal

$$\frac{1}{236{\cdot}22} = 0{\cdot}004233,$$

consequently greater than the expansion of air, as was to be expected. This coefficient is now determined for the first time, it awaits its confirmation by experiment.

The accuracy to which this determination lays claim must not be overrated. The formula (2.) in No. 15 is so plastic, that the number 336·22 may be altered by several units without a corresponding change being made in B, the differences of the results of the formula from those of observation becoming considerably larger, so that the coefficient of expansion, such as was given, appears to be trustworthy only to about $\frac{1}{100}$ of its value.

18. The density of steam is found with the coefficient of expansion α, as is known by the formula

$$\frac{\varrho}{\varrho'} = \frac{p}{p'} \cdot \frac{1 + \alpha t'}{1 + \alpha t}.$$

For $t' = 0$ (the boiling-point) and $p' = 1$ atmosphere $= p_0$ is, according to Gay-Lussac's determination,

$$\varrho' = \frac{1}{1{\cdot}6964},$$

consequently

$$\varrho = \frac{1}{1{\cdot}6964} \cdot \frac{336{\cdot}22}{336{\cdot}22 + t} \cdot \frac{p}{p_0}, \quad \ldots \quad (4.)$$

in which p is the pressure and t the temperature of the steam.

If it be desired, as is generally done, to take the temperature from the freezing-point of water, we have

$$\varrho = \frac{1}{1{\cdot}6964} \cdot \frac{336{\cdot}22}{236{\cdot}22 + t} \cdot \frac{p}{p_0}$$

$$= \frac{198{\cdot}19}{236{\cdot}22 + t} \cdot \frac{p}{p_0}. \quad \ldots \quad (5.)$$

The density of the atmospheric air is, under the same circumstances,

$$\varrho_1 = \frac{1{\cdot}299}{1 + 0{\cdot}003668\,.\,t} \cdot \frac{p}{p_0}.$$

The density of steam compared to that of atmospheric air of equal temperature and pressure is therefore

$$\frac{198{\cdot}19}{1{\cdot}299} \cdot \frac{1 + 0{\cdot}003668\,.\,t}{236{\cdot}22 + t},$$

or

$$= 0{\cdot}55964 \,.\, \frac{272{\cdot}63 + t}{236{\cdot}22 + t} \quad \ldots\ldots \quad (6.)$$

for which may be substituted with lower temperatures the approximate formula

$$0{\cdot}6459\,.\,(1 - 0{\cdot}000652\,.\,t). \quad \ldots\ldots \quad (7).$$

Consequently at 0° the density of steam is to that of air as 1 to 0·6459. Munke* found for low temperatures, on an average, the density 0·6568, viz. $\frac{1}{1{\cdot}5324}$.

At 20° C. the density of steam is, according to formula (7.), equal 0·6329. Schmeddingk† obtained on an average for this temperature the density 0·63.

Finally, at 100° C. the density of steam is found to equal 0·6207 from the accurate formula (6.). The approximate formula gives in this case only 0·5807, and should consequently no longer be employed for such high temperatures. The density found approaches closely to that deduced from the chemical composition =0·6217, and differs from that of Gay-Lussac's determination only because in this place the coefficient of expansion 0·3668, discovered by Magnus, was employed instead of Gay-Lussac's 0·375.

I imagine that the coincidence with these three results of observation is as great as can be expected in such difficult determinations.

19. The coefficient $B = 5{\cdot}2555$ in the formulæ (2.) and in (3.) is equal to $M \,.\, \frac{a\,b}{k\,\alpha}$ (No. 15). In this

M is the modulus of Briggs's logarithms.

a the mechanical action which the unit of heat is capable of producing = 374 (No. 8).

* Gehler's *Wörterbuch*. Neue Bearb. x. Wärme, S. 1100.

† Dove, *Repertorium der Physik*, 1. S. 52.

α the expansion for 1° C., in this case $\frac{1}{336{\cdot}22}$, if we set out from the volume at boiling-point.

k is determined by the formula

$$p = k\varrho(1 + \alpha t).$$

For the boiling-point $t = 0$, and under the pressure of one atmosphere ($p = 10333$ kilogrammes), the density of the steam $= \frac{1}{1{\cdot}6964}$, therefore $k = 10333 \times 1{\cdot}6964 = 1{\cdot}7529$.

b is the specific heat with constant pressure when this pressure amounts to *one* atmosphere (7.), referred to the unit of weight. This specific heat may therefore be calculated from the known value of B; we have

$$b = \frac{5{\cdot}2555 \,.\, k\alpha}{Ma},$$

which, with the numbers just established, gives

$$b = 1{\cdot}6869.$$

20. The difference of the specific heats with constant pressure and constant volume is, according to II. in No. 5, $= \frac{k\alpha}{a}$; consequently in this case $= 0{\cdot}1394$. Consequently *the specific heat of steam* under the pressure of one atmosphere is, the pressure being constant, $= 1{\cdot}6869$, and, the volume being constant, $= 1{\cdot}5475$.

The ratio of one to the other is 1·0901. For any pressure p,

$$\left.\begin{aligned} c &= 1{\cdot}687 - 0{\cdot}321 \,.\, \log\frac{p}{p_0}, \\ c_1 &= 1{\cdot}548 - 0{\cdot}321 \,.\, \log\frac{p}{p_0}. \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (8.)$$

The logarithms are Briggs's, and the specific heats refer to units of weight.

The limit c_1, equal to 0 (see No. 12), makes its appearance here very late, viz. at a pressure approaching closely to 100,000 atmospheres.

21. There are very few experiments with the results of which the values here found might be compared, and even these deserve but little confidence. Benzenberg has found the velocity of sound in steam nearly equal to that which results from Newton's formula. This indicates that $\frac{c}{c_1}$ must be very nearly $= 1$.

The experiments of Van Rees are more accurate; he finds*, with an external temperature of 10°·6 from the relations of sound of a pipe which was first blown into with air and then with steam, the velocity of sound in steam to equal $369^{m}{\cdot}6$ reduced to 0°, in which the velocity of sound in the atmosphere is assumed to be $333^{m}{\cdot}7$. From these numbers there results, calculated in the way Dulong has done, the relation $\frac{c}{c_1} = 1{\cdot}1213$ with the above found density of steam.

But this number still requires a correction. Van Rees has reduced the velocity of the steam to 0° with Gay-Lussac's coefficient, 0·00375. If, instead of this, the one found by me, 0·004233, be employed, we have, since the temperature of the steam was certainly very near 100° (it is not stated in the work quoted), to multiply the above result by $\frac{1{\cdot}375}{1{\cdot}4233}$. We then obtain

$$\frac{c}{c_1} = 1{\cdot}0831,$$

which agrees more closely with my determination 1·0901 than was to be expected, considering the nature of these experiments, and the uncertainty still prevailing respecting the above calculated value of a.

22. De la Roche and Bérard have attempted to determine the specific heat of steam. They caused air which had been saturated with steam at 39°† to cool in higher degrees of temperature, at about 56°, and observed how much heat was given off.

The pressure under which the moist air stood was $0^{m}{\cdot}7596$
Steam has at 39° the force of tension . . . . . $0^{m}{\cdot}0521$
There consequently remains the pressure of dry air $0^{m}{\cdot}7075$

The quantity of heat in the air for this pressure is (No. 9 and 13)

$$q = A + 0{\cdot}267\,.\,t - 0{\cdot}180\,.\left\{\frac{1}{\alpha} + t\right\}.\log\frac{0{\cdot}7075}{0{\cdot}7600}$$

$$= A + 0{\cdot}273\,.\,t + 0{\cdot}0055\,.\,\frac{1}{\alpha}.$$

This air was cooled 56°. In this operation it gives off the heat $0{\cdot}273\,.\,56 = 15{\cdot}29$.

At the same time an equal volume of steam is cooled the same

* Gehler's *Wörterbuch*, a. B. viii. Schall. St. 478.

† These statements are taken from Gehler's *Wörterbuch*, vol. x. Heat, Part 693.

number of degrees. The quantity of heat in $1^{kil.}$ steam of the presures 0·0521 is

$$q = A + 1{\cdot}687\,.\,t - 0{\cdot}321\left\{\frac{1}{\alpha} + t\right\}.\log\frac{0{\cdot}0521}{0{\cdot}7600}$$

$$= A + 2{\cdot}060\,.\,t + 0{\cdot}373\,.\,\frac{1}{\alpha},$$

and the quantity of heat given off in cooling 56° equals 2·060 . 56 = 115·36.

The density of this steam is to that of air of the same force of expansion at the temperature 30°, about $\frac{5}{8}$, and to air under the pressure $0^{m.}7075$ equal $\frac{5}{8}\cdot\frac{0{\cdot}0521}{0{\cdot}7075} = 0{\cdot}0460$, with $1^{kil.}$ air only $0^{kil.}0460$ steam is cooled; the heat which is given off is therefore

$$15{\cdot}29 + 0{\cdot}0460 \times 115{\cdot}36 = 20{\cdot}57.$$

In an experiment with dry air this was cooled 56°·9; it likewise stood under the pressure $0^{m.}7596$; the quantity of heat given off by $1^{kil.}$ of this air is $0{\cdot}267 \times 56{\cdot}9 = 15{\cdot}18$. This air was in the proportion $\frac{0{\cdot}7596}{0{\cdot}7075}$ denser than that in the first experiment; consequently if the velocity of the air in both had been the same, there would have passed through the pipe during the time, in the one, $1^{kil.}$ dry air, in the other, $\frac{0{\cdot}7596}{0{\cdot}7075} = 1^{kil.}074$, and would have given off $1{\cdot}074 \times 15{\cdot}18 = 16{\cdot}30$ heat.

According to this calculation the increments of heat should stand in the two experiments in the proportion 20·57 : 16·30, or 9·5 : 7·52; but the observed were 9·5 and 8·6; the difference amounts to 1°·08, and is more considerable than can be explained from the uncertainty of the numbers here employed for the calculation. But assuredly the sources of error in this experiment are far more considerable than in the other experiments of De la Roche and Bérard, and the appearance of so great a difference will be explained from their consideration, combined with the accuracy above noticed of the numbers employed by me.

§ 4. *Specific Heat and Elasticity of other Vapours.*

23. The formula (2.) in No. 15 furnishes in like manner the elasticity of other vapours, if B and $\frac{1}{\alpha}$ are determined for these

vapours, and the temperature t is reckoned from the boiling-point of the fluid under consideration. Higher temperatures must in such case be indicated according to the air thermometer.

24. For the *vapour of mercury* I obtain with the results of the experiment of Avogadro* the formula,

$$\log \frac{p}{p_0} = \frac{2{\cdot}0089 \,.\, t}{348 + t}, \quad \ldots\ldots\ldots \quad (9.)$$

in which the temperatures are reckoned from 350°, and p_0 represents, as previously, the pressure of one atmosphere. A comparison of the direct observations with the results deduced from this formula is contained in the following table:—

Force of expansion in millimetres.	Values of t.		Observed temperatures, starting from freezing-point.		Difference between 2 and 3.
	Calculated.	Observed.	Air thermom.	Merc. thermom.	
58·01	−124·37	−124·1	225·9	230	+0·27
80·02	−113·92	−114·5	235·5	240	−0·58
105·88	−103·98	−104·95	245·05	250	−1·03
133·62	− 95·06	− 95·4	254·6	260	−0·34
165·22	− 86·33	− 85·9	264·1	270	+0·43
207·59	− 76·24	− 76·3	273·7	280	−0·06
252·51	− 66·95	− 66·8	283·2	290	+0·15

The coincidence is, as is seen, satisfactory.

25. From this formula results, first, the limit of evaporation $= -348°$, *i. e.* this limit is situated 2° above the freezing-point of water. This coincides with the observation of Faraday, who perceived no mercurial vapour below 0°.

26. The expansion of the vapour of mercury amounts, if we start from the volume which it has at the boiling-point of mercury, to $\frac{1}{348}$, or 0·00259 of its volume for every centigrade degree.

27. The coefficient 2·0089 is in the former notation (see 19), equal $M \,.\, \frac{a\,b}{k\,\alpha}$. In this $a = 374$; $\frac{1}{\alpha} = 348$; and k is found from the statement, that at the boiling-point the vapour is 6·9785 times as dense as air of the same temperature, equal

$$\frac{10333\,(1 + 350 \times 0{\cdot}003668)}{1{\cdot}299 \,.\, 6{\cdot}9785} = 2602.$$

We thus finally obtain b, *i. e. the specific heat of mercurial va-*

* Dove, *Repertorium der Physik*, i. Part 53.

pour under the pressure of one atmosphere, referred to the unit of weight = 0·09248.

Referred to the same volume at the boiling-point of mercury, this specific heat is compared with that of atmospheric air,

$$\frac{6{\cdot}9785 \times 0{\cdot}09248}{0{\cdot}267} = 2{\cdot}04.$$

The difference of the specific heats, pressure and volume being constant, is $\frac{k\alpha}{a} = 0{\cdot}01999$; consequently the specific heat with constant volume referred to the unit of weight = 0·07249, and the relation of both = 1·275.

28. From the observations of Marx, I find the boiling-point of the *sulphuret of carbon* with a pressure of 0m·76 = 336·905 Paris lines = 37°·83 R. If the temperatures are reckoned from this point, I obtain the formula

$$\log \frac{p}{p_0} = \frac{4{\cdot}7126 \,.\, t}{268{\cdot}8 + t}. \quad . \quad . \quad . \quad . \quad . \quad (10.)$$

It affords the following comparison with the observed values:—

p in Paris lines.	t		Difference.	Observed temperature setting out from 0°.
	Calculated.	Observed.		
32·00	−47·92	−44·83	+3·09	− 7° R.
58·50	−37·34	−37·83	−0·49	0
96·92	−27·74	−27·83	−0·09	10
156·25	−17·78	−17·83	−0·05	20
243·13	− 7·84	− 7·83	+0·01	30
367·62	+ 2·18	+ 2·17	−0·01	40
494·00	+ 9·83	+ 9·67	−0·16	47·5

The coincidence is, with the exception of the two first values, certainly greater than the errors of the observations themselves. The observed heights of the mercurial columns are not reduced to one temperature, on which account this expression has less value than the previous ones. I therefore pass over further calculations from the formula; it is for centigrade degrees,

$$\log \frac{p}{p_0} = \frac{4{\cdot}7126 \,.\, t}{336 + t},$$

in which the temperatures must then be counted from 47°·27 C.

29. Bunsen* has published an account of the elastic forces calculated by him from experiments of *sulphurous acid.* They

* Poggendorff's *Annalen*, xlvi. 97.

give the formula

$$\log \frac{p}{0{\cdot}78} = \frac{5{\cdot}866\,.\,t}{232{\cdot}2+t}, \quad \ldots\ldots \quad (11.)$$

in which the force of expansion is measured by the height of a column of mercury in metres, and t should be reckoned from $-10°$ C. The following table exhibits the comparisons of this formula with the forces of expansion calculated by Bunsen.

Temperature.		Elastic force in Metres.		Difference.
Degree C.	t.	Formula.	Bunsen.	
−10	0	0·78	0·78	
− 5	5	1·04	1·11	+0·07
0	10	1·36	1·48	+0·12
+ 5	15	1·77	1·91	+0·14
10	20	2·28	2·39	+0·11
15	25	2·90	2·93	+0·03
20	30	3·66	3·54	−0·12
25	35	4·56	4·20	−0·36

The differences are large, but yet not too large for pressures measured with an air manometer; the more so as the numbers given by Bunsen appear to have been found by interpolation. Probably the pressure 0·78, upon which I based my calculation, is somewhat too small, which would render the formula better for representing the course of the elasticities.

For the temperature at which the pressure becomes $0^{m}{\cdot}76$, we find $t=-0{\cdot}447$, which gives for the boiling-point of sulphurous acid $-10°{\cdot}447$ C. Bunsen found with the pressure $0^{m}{\cdot}744$ the boiling-point $-10°{\cdot}5$ C *.

30. The expansion of the unit of volume at 0° C. is, according to the above, $\frac{1}{242{\cdot}2}=0{\cdot}00413$, when the gas stands, according to the above table, under a pressure of $1^{m}{\cdot}48$, therefore near two atmospheres. According to Magnus the expansion is 0·003859 under the pressure of one atmosphere; and from Regnault's experiments it results that this expansion increases with the pressure, so that the coefficient of expansion now found has great probability under those conditions for which it obtains.

31. For the maximum of the elastic force of *cyanogen gas* I find likewise from Bunsen's statements, the formula

* I found this statement only after I had already made this calculation; it gives indeed the best datum for the calculation of the coefficients of the formula. I did not however feel inclined to repeat the tedious calculation, as it could only yield a slightly different result.

$$\log \frac{p}{0{\cdot}75} = \frac{5{\cdot}44 \,.\, t}{258 + t}, \quad \ldots\ldots \quad (12.)$$

in which p is expressed in metres and t is counted from $-20°{\cdot}7$ C., the boiling-point observed by Bunsen with the pressure $0^{m}{\cdot}75$. We obtain with it

Temperature.		Elastic force in Metres.		Difference.
Degree C.	t.	Formula.	Bunsen.	
−20	0·7	0·78	0·80	+0·02
−15	5·7	0·98	1·10	+0·12
−10	10·7	1·23	1·41	+0·18
− 5	15·7	1·54	1·73	+0·19
0	20·7	1·90	2·07	+0·17
5	25·7	2·33	2·44	+0·11
10	30·7	2·84	2·88	+0·04
15	35·7	3·44	3·33	−0·11
20	40·7	4·13	3·80	−0·33

The boiling-point for the pressure $0^{m}{\cdot}76$ results from the above formula for $t = 1{\cdot}67$, therefore at $-19°{\cdot}03$ C.

32. The expansion of the unit of volume at 0° amounts, according to the advanced formula for each degree C., to

$$\frac{1}{279} = 0{\cdot}00359.$$

Regnault states this expansion at 0·003682. Both statements agree in so far as the number 279 is trustworthy (see No. 17).

33. Bunsen finds the boiling-point of *ammonia* at the pressure of $0^{m}{\cdot}7493$ to equal $-33°{\cdot}7$. If the temperatures are measured from this point, the greatest force of expansion of ammonia in metres of mercury is obtained from the formula

$$\log \frac{p}{0{\cdot}7493} = \frac{5{\cdot}24 \,.\, t}{230 + t}. \quad \ldots\ldots \quad (13.)$$

From this formula we find the forces of expansion calculated in the following table.

Temperature.		Elastic force in Metres.		Difference.
Degree C.	t.	Formula.	Bunsen.	
− 5	28·7	2·86	3·04	+0·18
0	33·7	3·49	3·61	+0·12
+ 5	38·7	4·27	4·26	−0·01
10	43·7	5·12	4·98	−0·14
15	48·7	6·15	5·78	−0·37
20	53·7	7·35	6·67	−0·68

The boiling-point for the pressure $0^{m}{\cdot}76$ is found, according to the above formula, at $t = +0{\cdot}26$, therefore at $-33°{\cdot}44$ C.

34. The expansion of the unit of volume at $-33°{\cdot}7$ amounts for each degree of heat, according to the above formula, to $\frac{1}{230}$, therefore $\frac{1}{230+33{\cdot}7}=\frac{1}{263{\cdot}7}=0{\cdot}00379$ of the volume at 0°. Regnault has examined this expansion, but obtained no results which he considers trustworthy; they are 0·00370, 0·00371, and 0·00373.

35. It has been frequently advanced as probable that gases under corresponding conditions experience the same expansion by heat. Let us see how far the results here obtained support this proposition. It is undoubtedly requisite to regard as corresponding conditions those in which gases have attained a certain pressure as maximum of their tension with the temperature present, or for instance the boiling-points of the liquids condensed from the gases or vapours under the pressure $0^{m}{\cdot}76$.

If we refer the expansion on the raising of the temperature 1° C. to the unit of volume with the boiling-point of the liquid under consideration, the following comparison results from the preceding:—

Liquid.	Boiling point.	Expansion of the vapour for 1° C.
Water.....	100°	$\frac{1}{336{\cdot}22}=0{\cdot}00297$
Mercury	350	$\frac{1}{348}=0{\cdot}00259$
Sulphuret of carbon.	47·29	$\frac{1}{336}=0{\cdot}00298$
Sulphurous acid.....	−10·45	$\frac{1}{232}=0{\cdot}00432$
Cyanogen	−19·03	$\frac{1}{260}=0{\cdot}00385$
Ammonia	−33·44	$\frac{1}{264}=0{\cdot}00378$

It will be seen that this comparison is by no means favourable to that view. And moreover the expansion of the atmospheric air amounts to 0·003668 of the volume at 0°, that is $\frac{1}{273}$, and it then becomes $\frac{1}{336}$, as in steam and sulphuret of carbon, when the expansion is referred to the volume of air at $336-273=63°$, when, if the above view were correct, atmospheric air would be-

come liquid under the pressure $0^{m}{\cdot}76$! This view must consequently be modified, or the definition of what are termed corresponding conditions altered.

§ 5. *Principles of the Theory of Steam-Engines.*

36. If a kilogramme of a liquid at the temperature t is converted into vapour of the temperature t, a certain quantity of heat is requisite, which is termed the *latent heat* of the vapour. The action of this heat consists in the overcoming of the cohesion of the fluid, and in this that a pressure equal to the force of expansion of the vapours is forced back through a certain space.

If we imagine, as in No. 3, a cylindrical vessel in a vertical position of 1^{mq} section, and in this the fluid, the temperature of which shall be t; above it a moveable piston, which is held down by a weight p, equal to the pressure of the vapours of t° on 1^{mq}, then it will be seen that on the further addition of heat to the fluid it boils, and the generated vapour pushes up the piston, therefore the weight p is raised. Now if $\Delta^{kil.}$ represent the weight of 1^{mc} of the fluid at t°, $\varrho^{kil.}$ the weight of 1^{mc} of the vapours at t° and the pressure p, then $1^{kil.}$ of the fluid occupies the space $\frac{1}{\Delta}$, or the height $\frac{1}{\Delta}$ in the aforesaid cylinder; the vapours produced from it likewise occupy the space $\frac{1}{\varrho}$, or the height $\frac{1}{\varrho}$. Consequently the weight p pressing on the piston has been raised by the formation of the vapours to the height $\frac{1}{\varrho} - \frac{1}{\Delta}$, therefore the mechanical force

$$p\left\{\frac{1}{\varrho} - \frac{1}{\Delta}\right\}$$

has been generated.

This mechanical force + that entirely unknown to us, which is equivalent to the destruction of the cohesion, and which I will designate by C, is the effect of the added, *i. e.* of the latent heat. Multiplied with the mechanical action of the unit of heat, it must be equal to this. If the latent heat be w, and a, as previously, the mechanical force of the unit of heat, then

$$w \,.\, a = p\left\{\frac{1}{\varrho} - \frac{1}{\Delta}\right\} + \mathrm{C}. \quad . \quad . \quad . \quad . \quad (1.)$$

In most cases $\frac{1}{\Delta}$ may be neglected in comparison with $\frac{1}{\varrho}$, it then becomes more simple,

$$w \cdot a = \frac{p}{\varrho} + C,$$

or
$$w \cdot a = k(1 + \alpha t) + C. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

37. The quantity of heat which is required to overcome the cohesion results from

$$\frac{C}{a} = w - \frac{k(1 + \alpha t)}{a}.$$

According to the assumption made in No. 15, if, at the same time, it be admitted that the specific heat of the liquid be constant and $= s$, we have

$$w = w_0 - s\,t,$$

where w_0 is the latent heat of the vapour of the temperature $t = 0$. We then have

$$\frac{C}{a} = w_0 - s\,t - \frac{k(1 + \alpha t)}{a}. \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

The heat which destroys the cohesion of the liquid consequently decreases with the temperature.

For water, $w_0 = 640$, according to Brix, if we set out from 0° C.; $s = 1$; $\frac{k\alpha}{a} = 0{\cdot}1394$ (No. 20); $\frac{1}{\alpha} = 236$ (No. 17).

Consequently the heat requisite for the suspension of the cohesion of water, or *the cohesion of water* itself, is

$$640 - t - 0{\cdot}1394\,(236 + t) = 607 - 1{\cdot}1394\,.\,t. \quad . \quad (4.)$$

The action of this quantity of heat is lost in all steam-engines, which hitherto has been wholly overlooked; this loss amounts, as is evident, to much less at high temperatures than at low ones, whence it results that attention must be directed far more than hitherto to the construction of steam-engines with very high pressure.

The quantity of heat required, according to formula (4.), for the overcoming of the cohesion of steam amounts for 1 kilogram. water with

$t =$	0	100°	200°	400°	533°
$t_0 =$	607	493	379	151	0

units of heat.

38. Of the 640 units of heat required for the production of 1 kilogram. steam, t of them are required to heat the water, and only

$$33 + 0{\cdot}1394\,.\,t$$

generate a force, and *the mechanical action which is obtained according to theory from* 1 *kilogram. of steam which had formed at* t° *Cent. amounts, when no expansion occurs, but a perfect condensation takes place, to*

$$374\ (33 + 0{\cdot}1394\ .\ t) = 12300 + 52{\cdot}1\ .\ t. \quad . \quad . \quad (5.)$$

This power consequently increases very rapidly for engines which work with high temperatures. It is measured as before by kilogrammes, which are raised 1 metre.

The coefficient 374, which now occurs, is the mechanical force of the unit of heat (No. 8).

39. An entire condensation never occurs; if it takes place at t_1 degrees, it should be deducted from the above amount of power, which would have been yielded by the formation of a volume of steam of t_1 degrees equal to that then existing.

If p be the pressure and ϱ the density of the steam at t degrees, and p_1 the pressure of the steam at t_1 degrees, then the action which is obtained by the formation of 1 kilogramme of steam in the first case is $\frac{p}{\varrho}$, which, with the value of ϱ in the formula (5.), No. 18, again gives the value just found, $12300 + 52{\cdot}1\ .\ t$. Upon the other side of the piston the pressure p_1 must be forced just as far back, which requires the power $\frac{p_1}{\varrho}$, or $\frac{p_1}{p}\ (12300 + 52{\cdot}1\ t)$, *there consequently remains for the duty of the engine,*

$$\left\{1 - \frac{p_1}{p}\right\} (12300 + 52{\cdot}1\ .\ t). \quad . \quad . \quad . \quad (6.)$$

The relation $\frac{p_1}{p}$ might likewise be expressed with the aid of the formulæ previously given for t and t_1.

For a low pressure engine t is about 107; $p = 950^{\text{kil.}}$, and for $t_1 = 50^{\circ}$, $p_1 = 89$; with this the theoretical duty for every kilogramme of water converted into steam becomes equal to 16200^{km}. For a one-horse power (75^{km} in 1 sec.) there must consequently only be 17 kilogrammes of water converted into steam in one hour, and therefore about $2\frac{5}{6}$ kilogrammes of coals should be consumed; while usually with such engines from 5 to 6 kilogrammes of coals are required for the hour and horse power, so that the theoretical effect here calculated is about twice as great as that obtained in reality.

But the duty which may be obtained according to theory from 640 units of heat at the maximum, amounts to 640×374

$=239400^{km}$, and of this the above calculated theoretical duty of the low pressure engine is only the fourteenth part, and the mechanical force really obtained only the twenty-eighth.

40. The calculation of the theoretical effect of the expansion-engine now likewise becomes very simple. If with any pressure p, v is the volume which $1^{kil.}$ steam occupies, ϱ the weight of 1 cubic metre of this steam, and t its temperature, then $p\,dv$ is the duty which the steam yields on its expansion dv. This duty is, as in No. 3, equal

$$-\frac{p.d\varrho}{\varrho^2}.$$

With this expansion the steam retains its quantity of heat, its temperature sinks, and the temperature passes over into its equivalent mechanical force. Since the steam retains its quantity of heat, we have during the expansion,

$$\text{NL}\frac{p}{p_0}=\frac{ab}{k}\cdot\frac{t}{1+\alpha t}\text{ (No. 15.)},$$

and

$$\frac{dp}{p}=\frac{ab}{k\alpha}\cdot\frac{dt}{(1+\alpha t)^2}.$$

Moreover, the three quantities, p, ϱ and t, are combined by the equation

$$p=k\varrho(1+\alpha t);$$

whence results

$$d\varrho=\frac{\frac{dp}{dt}}{k(1+\alpha t)}\cdot dt-\frac{p\alpha}{k(1+\alpha t)^2}\cdot dt.$$

If we substitute in this expression $\frac{dp}{dt}$ from the preceding, and lastly substitute this value of $d\varrho$ in the expression of the mechanical action above calculated, we obtain, after some simple reductions, the mechanical force for the change of the temperature t by dt equal

$$\left\{-\frac{ab}{1+\alpha t}+\alpha k\right\}.dt,$$

the integral of which

$$-\frac{ab}{\alpha}.\text{NL}(1+\alpha t)+\alpha k t+\text{Const.}$$

If the change of temperature commences at the temperature t_1, and proceeds until the temperature becomes t_2, then *the mechanical force during the expansion of* 1 *kilogramme of steam is*

$$\frac{a\,b}{\alpha} \cdot \mathrm{NL}\frac{1+\alpha t_1}{1+\alpha t_2} - \alpha k (t_1 - t_2),$$

or, with the above determined values of a, b, α and k,

$$488000 \cdot \log \text{Briggs}\frac{236+t_1}{236+t_2} - 52{\cdot}14\,(t_1 - t_2), \quad . \quad . \quad (7.)$$

where the temperatures are reckoned from 0° Cent.

41. If after this expansion the steam is condensed at t_3 degree, the duty thereby lost, as in No. 39, is equal to

$$\frac{p_3}{p_2}(12300 + 52{\cdot}1 \cdot t_2),$$

in which p_3 and p_2 are the forces of expansion of the steam of t_3 and t_2 degrees. From (5.), (7.), and this expression, finally *the duty of the steam-engine with expansion and condensation for* 1 *kilogramme of steam*, is equal to

$$12300 + 52{\cdot}1 \cdot t_1 + 488000 \cdot \log\frac{236+t_1}{236+t_2} - 52{\cdot}1\,(t_1 - t_2) -$$

$$- \frac{p_3}{p_2}(12300 + 52{\cdot}1 \cdot t_2) =$$

$$= (12300 + 52{\cdot}1 \cdot t_2)\left\{1 - \frac{p_3}{p_2}\right\} + 488000 \cdot \log\frac{236+t_1}{236+t_2}. \quad (8.)$$

For an engine in which the steam had originally the temperature 140° ($3\frac{1}{2}$ atmospheres), then by expansion falls to 40°, and is also condensed at this temperature, we obtained the theoretical duty for 1 kilogramme of the produced steam equal 65450 kilometres.

There has been obtained with high pressure with expansion and condensation the duty 19800^{km} from 1 kilogramme of coals, therefore for 1 kil. steam about $\frac{1}{6}$th of this, or 33000^{km}, which is somewhat more than the half of the theoretical maximum just calculated. But even this theoretical maximum is only the $\frac{239400}{65430}$, or about the fourth part of the duty which the heat absorbed by the water should yield.

A far greater portion of the motive force of the heat is likewise obtained with these engines on employing steam of very high temperature.

Article VIII.

Experiments on the Expansive Force of Steam. By Professor Gustav Magnus*.

[From Poggendorff's *Annalen*, No. 2. for 1844.]

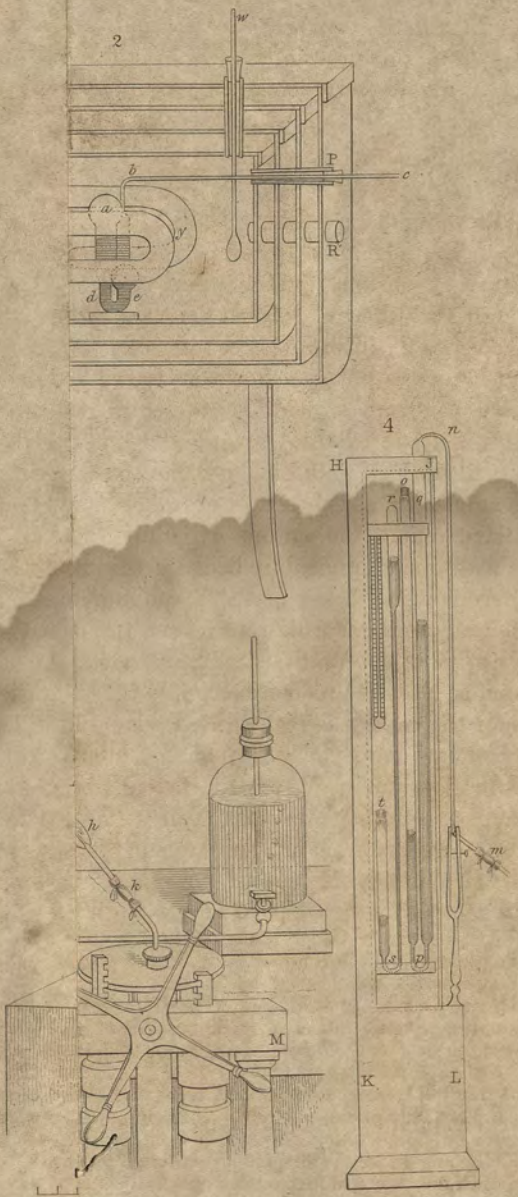
In a former memoir† I have shown that the various gases have not, as was previously believed, the same, but different coefficients of expansion. It is therefore probable that the coefficient of expansion hitherto admitted for steam is likewise not correct, and it appeared to me of great interest to ascertain this accurately. For this purpose, however, it was requisite to know the pressure of steam at various temperatures, especially between 0° cent. and 100°. On perusing the investigations which had been made on this subject, I became convinced that I could lay down none of them as bases for my experiments, not only because the statements of the various experimenters do not sufficiently agree with one another, but because the methods employed by them are far from being perfect; and moreover, because in none of the investigations which have been published on this subject are the original observations communicated. All of them, indeed, contain, at least the recent ones, only the expansive forces calculated for the entire degree, which necessarily differ according to the formula employed for their calculation‡. Since we are moreover ignorant how far the actual observations differ from the values found by interpolation, it is impossible to judge what degree of accuracy the existing statements possess. I therefore resolved to submit this subject to a new investigation.

The methods which have hitherto been employed to measure

* Translated from the German by W. Francis, Ph. D., F.L.S.

† Poggendorff's *Annalen*, vol. lvii. p. 177.

‡ The table contained at the end of the first volume of Biot's *Traité de Physique*, on the expansive forces of steam between 0° and 100°, which is copied in nearly all the French Manuals on Natural Philosophy, is calculated according to Dalton's statements. (Biot's *Traité*, i. p. 272.) But these themselves are the result of a calculation, and in fact according to quite a different formula, and are only partially founded on direct measurements of the expansive forces in a barometer tube, and partially on the observation of the temperature of water boiling under the air-pump at different pressures. Moreover, Dalton has considerably modified these statements in the second edition of his 'System of Chemical Philosophy.'



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the pressure of steam are founded either on the determination of the temperature at which water boils under various pressures, or on the bringing of water into a perfect or nearly perfect vacuum, exposing it to different temperatures and measuring the pressure which its vapour exerted.

The first of these two methods has been executed sometimes by observing the temperature at which water boils on high mountains, sometimes by boiling it under the recipient of the air-pump. This latter mode of inquiry, according to which experiments have been made by Achard*, Gren†, and likewise by Dalton‡, can only yield approximately accurate results, since when water boils under the air-pump its temperature constantly decreases, as well as the expansive force of the vapour. The observation of the boiling-point on high mountains may on the contrary lead, when carefully performed, to perfectly certain determinations. However, of this kind we unfortunately possess only older observations, with the exception of a very recent treatise by Forbes§. The first who made such observations was probably Le Monier||, who at Perpignan, in 1739, immersed a thermometer graduated at 28 inches 2 lines in boiling water on the Canigou in the Pyrenees. The barometer stood only at 20 inches $2\frac{1}{2}$ lines, and corresponding, the thermometer likewise stood 15° Delisle's or 9° R. lower than at Perpignan. Subsequently, in the years 1762 and 1770, De Luc** made several series of such observations on the Alps. He employed a thermometer which had been graduated at a barometric height of 27 inches. Gren†† has on that account reduced the statements to a thermometer graduated at 28 inches. These observations, however, as well as a couple by Saussure‡‡, made in his journey through the Alps, have not been performed with all the requisite measures of precaution, and consequently have not led to any accurate results.

Most of the investigations on the expansive force of steam

* Achard, *Sammlung physikalischer und chemischer Schriften*, i. 213; likewise in the *Schriften der Berliner Akademie*, 1782, p. 3.

† *Neues Journal*, i. 184.

‡ Memoirs of the Literary and Philosophical Society of Manchester, vol. v. part 2. p. 535.

§ Transactions of the Royal Society of Edinburgh, vol. xv. part 3. p. 409.

|| As stated by Cassini de Thury in the *Mémoires de l'Académie*, 1740, p. 92.

** *Recherches sur l'Atmosphère*, ii. 285. and iv. 143.

†† Gren's *Neues Journal der Physik*, i. 179.

‡‡ Saussure, *Voyage*, § 1275 and 2011.

have been made by measuring the pressure which vapour exerts in a confined space. Either the steam has been allowed to act against a piston, as in the researches of Christian*, and the weight determined which it was capable of raising at different temperatures, or, as in those of Arzberger†, the force measured with which the steam at various pressures raised a globular valve. Such experiments can only be employed to ascertain the expansive force for temperatures above 100°, and moreover can only be of importance for the practical arts. And lastly, the expansive force of steam has been measured by the height of a column of mercury holding this expansive force in equilibrium.

Ziegler‡ was the first who performed some experiments in this manner, and published them in the year 1768; they are however very deficient, and bear in this respect no comparison with those made by Watt at Glasgow in the winter of 1764–65, which, however, were published by him at a far later period (1814) as an Appendix to the article Steam in Brewster's edition of Robison's 'System of Mechanical Philosophy'§. Similar investigations exist by Robison‖, Betancourt**, G. G. Schmidt††, Biker of Rotterdam‡‡, Southern§§, Dalton‖‖ and Ure***; and moreover some isolated observations by Gay-Lussac†††, August‡‡‡ and others, as well as some determinations of the expansive forces at low temperatures by Kämtz§§§, Prinsep‖‖‖‖ and others by comparison of barometers, one of which contained water in its vacuum.

The experiments of Biker were made only for temperatures higher than the boiling-point of water; those of Robison, Betancourt and G. G. Schmidt are older and less trustworthy, as is already evident, from their having assumed that steam at 0° had no expansive force. Such is not the case with respect to the experiments of Watt, Southern, Dalton and Ure; all four

* *Méchanique Industrielle*, ii. 225.
† *Jahrbücher des Polytechnischen Instituts in Wien*, i. 144.
‡ *Specimen Physico-chemicum de Digestore Papini*, p. 27.
§ Vol. ii. p. 29. ‖ *Ibid.* p. 23.
** *Mémoire sur la Force Expansive de la Vapeur.*
†† Gren's *Neues Journal*, iv. 151. ‡‡ Gilbert's *Annalen*, x. 257.
§§ In Robison's System of Mechanical Philosophy, ii. 170.
‖‖ Memoirs of the Literary and Philosophical Society of Manchester, v. part 2. p. 553; in his New System of Chemical Philososophy, second edit., 1827; and *Encyclopædia Britannica*, vol. xx. part 2. p. 599.
*** Phil. Trans. for 1818, p. 338. ††† Biot, *Traité de Phys.*, i. 287.
‡‡‡ Poggendorff's *Annalen*, v. 344. §§§ In his *Meteorologie*, i. 290.
‖‖‖‖ Journal of the Asiatic Society of Bengal for April 1833.

employed the same or nearly the same method; they introduced some water into the empty space of a barometer-tube, and warmed it by surrounding it with water. Watt and Southern employed for this purpose a metallic vessel, which was heated by a lamp, but this vessel does not always appear to have surrounded the entire portion of the barometer-tube filled with vapour; Dalton, on the contrary, fixed a wide glass tube by means of a couple of corks around the barometer-tube, and filled the intervening space with hot water. Biot however has already drawn attention to the fact, that in this method of Dalton's the surrounding water can scarcely have possessed the same temperature throughout its entire height, and has on that account advised inserting several thermometers in it at various depths. Ure considered it more advantageous to avoid this evil by the employment of a siphon-shaped barometer, the open branch of which was tolerably long; by filling it with mercury he succeeded in causing the vapour to occupy always the same space, even when their expansive force became greater. This space only occupied the length of half an inch in the apex of the barometer-tube, and he fixed the elongated bulb of his thermometer close to this space. He mentions, as a peculiar advantage which is gained by this method, that the mercury of the barometer-tube does not become unequally heated. I must however confess that I cannot conceive how this mercury, where it is in contact with the vapour, should not acquire nearly the same temperature which it possesses, and below that of the surrounding atmosphere. But a correction for the expansion of the mercury is not possible as long as the temperature is not the same throughout the whole height. Ure indeed appears to have felt that this was absolutely requisite; however, it is impossible to understand how he attained it in his method. I have consequently employed the following apparatus of measuring the expansive force of steam. It is, it is true, less simple, but I found it impossible to satisfy in any other way the above-mentioned requisite condition.

To measure the temperature, I preferred an air thermometer to the quicksilver thermometer, not merely on account of its greater sensitiveness, but especially because it admits of the employment of any arbitrarily great volume of air. It is thus possible to surround the space in which the vapour is contained almost entirely with this thermometric substance, and so to pre-

serve the temperature of this space itself more certain. The air thermometer is constructed exactly like the one I employed in my investigations on the gases and the comparison between the expansion of the air and of mercury. It is figured in Plate III. fig. 1, at D E. The tubes, however, which contained the air were of a different form and of greater capacity; their form is seen in fig. 2, where they are designated by X Y Z.

If the thermometer and the steam are to have exactly the same temperature, it is requisite that not only both be exposed to one and the same temperature, but that this remain constant for some time, otherwise there is no certainty that both the steam and the thermometer possess the same temperature at the moment of the observation, in case, for instance, the two do not become heated or cooled with the same rapidity. I employed on that account for the production of a constant temperature the same apparatus which I used in the comparison of the expansion of the air and of the mercury at high temperatures*. It is represented in figs. 1 and 2, designated with S P R, and consists of a case constructed of sheet-iron, surrounded by three other perfectly similar cases, so that between each two there exists a stratum of air $\frac{5}{9}$ths of an inch thick above as well as below and on every side. The cases are suspended in one another to avoid all metallic connexion in the lower portions. The outer case was heated by Argand's spirit lamps, of which I required only two in these experiments. When they burn with a moderate flame they constantly yield the same heat, and in this manner the air in the inner cases is kept at an invariable temperature.

M. Regnault has thrown out some suspicions as to the fitness of this arrangement†. He compared at the same time with me the expansion of air and of mercury at high temperatures, but arrived at different results to those which I obtained. He explains this difference by the unequal expansion of the glass, which he found might exert a very considerable influence‡. He also throws out suspicions as to the correctness of my experi-

* Poggendorff's *Annalen*, vol. lvii. p. 177.

† *Annales de Chim. et de Phys.*, 3rd series, vol. vi. p. 370.

‡ I cannot omit to notice in this place a blunder which occurs in an investigation which has the same object, viz. the comparison of quicksilver thermometers made of different glass, and which was executed by M. Pierre under the direction of M. Regnault in the laboratory of the Collège de France. M. Pierre has made the bulb of his thermometer of a different kind of glass from that of the tube (*Ann. de Chim. et de Phys.*, 3rd series, vol. v. p. 428), to which attention has already been drawn by Prof. Poggendorff in his translation of this

ments, intimating that the above-mentioned apparatus might easily lead to errors; I therefore felt it necessary to test it again before employing it in the present researches.

With this view I had made a second air thermometer of exactly the same construction as the former, with the exception that it contained the air in a vessel curved in the shape of a fork. The vessels of both thermometers were inserted in the apparatus in question, so that the one was exactly situated between the other forked one, and with it in the same horizontal plane, as exhibited in fig. 3. The following numbers are the temperatures which the two thermometers indicated on the contemporaneous application of heat.

Air Thermometer.

Vessel with two arms.	Vessel with one arm.	Difference.
158°·13	158°·18	+0°·05
187·79	187·96	+0·17
220·73	220·67	−0·06
287·60	288·14	+0·54

From this it is evident that the temperatures coincide as much as could be expected in these higher portions of the scale, consequently I did not object in the least to employ this apparatus for the contemporaneous heating of the vapours and air thermometer. It presents only *one* very great evil, which is, that it always requires several hours before the temperature in the inner case becomes constant, so that the experiments require a very great sacrifice of time.

The arrangement in which the vapour was generated consists of a short tube bent in the form of a U, and about four inches long, which is represented in *a b d e*, fig. 2. One of its extremities is closed, and in order to increase the space for the vapour blown out at *a* to a bulb. At the other extremity a glass tube *b c* is affixed at *b* at right angles, which passes through the envelope P of the case required for the heating and projecting from this as far as *c*. The short closed arm of this tube is filled with mercury which is well-boiled, then some water which had previously boiled violently without intermittence from half to three quarters of an hour was poured through *c* into the open arm, and a small quantity of it while still warm conveyed by in-

paper. It is scarcely necessary to mention, that in this case, on the application of heat, a tension must occur in the glass, and consequently an irregular expansion of the bulb.

clining the tube above the mercury. Upon this the remaining water is again poured out of the open arm, and what cannot be poured out on account of the form of the tube sucked up by a loose piece of string.

The portion of this arrangement projecting from the case is connected at *c* by means of caoutchouc with a glass tube *f g h k*, fig. 1, leading to an air-pump N M. When the air is rarefied, the vapour is able to overcome the pressure to which the water is subjected in the closed arm of the short U-shaped tube *a b d*, the mercury sinks in this and rises in the open arm.

The air is then rarefied until the surfaces of the mercury in both the arms are situated, at least approximatively, in the same horizontal plane. The small difference in height that may still exist is measured by means of a telescope, A B, fig. 1. With this view the case S P R is furnished with two tubes at R and R′ of $1\frac{1}{4}$ inch in diameter, which traverse all the cases, and are closed at both ends with glass discs, so that it is possible to see through them with the telescope. The tubes *a b d*, in which the vapour is formed, are so fixed to the inner case that the surfaces of the mercury lie exactly in the direction of these tubes.

The pressure of the rarefied air is indicated by the barometer attached to the air-pump; in order, however, to measure it more accurately, I employed a siphon gauge or metre of pressure, which is represented in fig. 4. It consists of a tube *o p q*, curved in the form of a U, 3 foot high, and half-filled with mercury; one of its arms is connected by tube *m l n*, fig. 1, with the exhausted space, while the other is open at *o*, or covered with a loosely-fitting cork. The difference in the height of the mercury in both arms was measured by means of the kathetometer, A B C, fig. 1.

To maintain the temperature of the mercury in this siphon gauge everywhere equal, it is surrounded with the case H I K L, one side of which is of wood, the other three of plate-glass, and which is easily closed at the top by a lid. It contains two thermometers, one at the bottom, the other at the top, of which I took the mean. In the same case was moreover fixed a siphon barometer *r s t*, which consequently had always the same temperature as the gauge, and was equally read off by means of the kathetometer.

The barometer had been compared with the normal barometer. Both the barometer and the gauge *o p q* had more than half

an inch internal diameter, so that no correction was requisite on account of capillary depression; the same was the case with the tube *a b d* in the box, the parts *a d* and *b e*, fig. 2, in which the surfaces of the mercury were preserved, being more than half an inch wide.

When I began these experiments, the mercury in the arm of the gauge *p q*, in which the air was rarefied, altered so much after a short time that it adhered to the sides, and its surface no longer reflected. I soon perceived that this change was caused by the aqueous vapour which got there on diluting and again letting in the air; on this account I inserted a chloride of calcium tube at *l m*, fig. 1, so that this evil was entirely avoided.

To avoid having to arrange the telescope of the kathetometer specially for each reading off, the various objects to be observed must be placed at equal distances from it. This equally refers to the tube *a b d* in the box, as well as to the gauge and the barometer. It would however have been difficult to have stationed the air thermometer at the same distance. In order to be able likewise to read this off by means of the kathetometer, I have applied to the object-glass of the telescope a convex glass, which may be readily prefixed. In this manner it was possible to observe the air thermometer, which was stationed nearer, without any further alteration in the telescope*.

The mode of proceeding in the experiments was as follows:—As soon as the temperature in the case P Q R had become constant, which was indicated by the air thermometer, and likewise by two quicksilver thermometers, *v* and *w*, fig. 1, affixed for this purpose, the air in the tubes *k c g b l n* was slowly rarefied. An assistant looked into the case and noticed when the mercury stood at the same height in both arms of the tube *a d b*.

An accident frequently occurred here which cost me much time and trouble; the tube, for instance, had always to be moved by knocking, in order that the water and mercury should become loosened in the closed arm of the glass, nevertheless it frequently could not be effected even when the rarefaction of the air had become several, sometimes even ten inches less than the expansive force of the vapour at the temperature existing. The

* It is indeed possible that by prefixing this glass the direction of the axis of the telescope is slightly altered; however, perfect parallelism is only requisite for the notations which are made either with prefixed glass, or for those made without it.

mercury then fell suddenly, the watery vapours were disengaged, and, as their expansive force was now greater than that of the rarefied air, they threw the mercury violently out of the tube *a b d*. Not only was the experiment rendered wholly valueless, but the tube *a b d* had to be replaced by a new one; and sometimes the mercury was projected with such force through the whole apparatus that it penetrated into the air-pump, so that this had to be taken immediately to pieces to preserve it from injury by amalgamation. To protect the air-pump from similar mishaps, I had a bulb blown in the tube *g k* at *h*, in which the tube *k h* terminated in a point curved upwardly. In this bulb the whole of the mercury must collect, however violently it might be projected into the tubes. I could however find no means of preventing the adhesion of the mercury and water in the boiled tube *a b d*. I introduced into it before it was curved a piece of polished iron wire, this floated after the mercury had been boiled and projected into the water, but even with this wire the same phænomenon resulted, only when a little bubble of air had collected above the water have I not observed it. I shall however subsequently recur to some conclusions drawn from this phænomenon.

If the mercury had sunk in the closed arm, some time elapsed before it acquired a constant position, evidently because the inner space had been cooled by the latent heat requisite for the formation of steam, and only gradually re-acquired the temperature of the surrounding medium. If the expansive force of the vapour was constant, the height of the air thermometer was read off by means of the kathetometer, then by means of the same instrument the difference between the heights in the tube *a b d* in the case, as well as the height of the water in the closed arm, and likewise the heights of the mercury in the gauge *o p q*, and the barometer *r s t*, fig. 1 and 4, measured.

One great advantage of the apparatus described consists in its being not only applicable to the measurement of pressures lower than the pressure of the atmosphere, but likewise for such as are higher. In this case it is only requisite to arrange the air-pump so that we can not only exhaust with it, but likewise condense, which the air-pumps commonly in use in this country, which are constructed with the so-called Grassmann's cock, readily admit of. The air is then condensed previously to the warming of the case S P R, and when the temperature has be-

come constant, air let out until its expansive force is equal to that of the steam. In this manner I have determined the expansive forces above 100° C. I was however compelled to arrange the caoutchouc-tubes so that they should not be blown out by the inner pressure. With the employment of the above-mentioned gauge, *o p q*, it would only have been possible to observe up to an expansive force of somewhat more than two atmospheres. To measure still higher expansive forces, it was only requisite to exchange the manometer for one in which the pressure is indicated by the changes in volume of a mass of air; it was also requisite to substitute solid metallic connections for those of caoutchouc and glass. The tube *a b d* in which the vapour is generated, as well as the tube of the manometer, can always be procured of sufficiently strong glass. This arrangement would then, in my opinion, deserve the preference to that employed by the French academicians* to measure the expansive forces at high temperatures; for this latter has, if I mistake not, yielded no perfectly accurate results, because the vapour, notwithstanding the measures of precaution taken, could not possess so high a temperature there, where it exerted its pressure, as in the boiler; but if the temperature of a space containing vapour differs at various places, its expansive force will always correspond only to the lowest, or at least to nearly the lowest temperature; and yet in the investigation by the academicians, only the temperature in the boiler, consequently only the highest existing, could be observed and laid down as a basis. Probably the differences between their results and those subsequently made by the Committee of the Franklin Institute in Pennsylvania†, are owing to this circumstance, although even in these latter the temperature in the boiler appears alone to have been measured.

The calculation of the expansive forces of steam from the observations obtained by means of the above-described apparatus is so simple that it scarcely requires mentioning; I will, however, give one example.

On the 16th of June, 1843, the barometer in the glass case H K L indicated $759{\cdot}4^{mm}$ at 20° C., and the gauge $436{\cdot}1^{mm}$; the difference consequently was $323{\cdot}3^{mm}$. These reduced to 0° give $322{\cdot}26^{mm}$ for the expansive force of the rarefied air. In the case the mercury in the arm of the tube *a b d*, in which

* *Ann. de Chim. et de Phys.*, vol. xliii. p. 274.

† *Encyclopædia Britannica*, vol. xx. p. 588. Steam.

was the vapour, stood 1·65^{mm} higher than in the other. To this is to be added the pressure which the water exerted in this arm; its height amounted to 2·65^{mm}, its pressure was consequently equal to a column of mercury of 0·20^{mm}, the expansive force of the vapour was consequently 1·85^{mm} less than that of the rarefied air, or = 320·41^{mm}.

The temperatures are referred to the absolute expansion of the air, and calculated from the indications of the air thermometer, according to the formula which I have given in the memoir on the expansion of air at high temperatures*, viz. retaining the symbols there selected:

$$\Theta = \frac{\frac{H' + h' - e}{H + h - e} - 1}{\alpha - \delta \frac{H' + h' - e}{H + h - e}}$$

in which Θ denotes the absolute expansion of the air expressed in degrees of the centesimal scale,

$H + h - e$ the elasticity of the air contained in the thermometer at 0°,

$H' + h' - e$ the elasticity of this air at the temperature Θ,

δ the expansion of the glass, and

α the absolute expansion of the air for 1° of the centesimal scale (in that memoir this was represented by $\frac{\alpha}{100}$).

The correction γ there applied is omitted because it has no perceptible influence for the temperatures now under consideration.

For the temperature 100° C. the boiling-point of water under the pressure 760^{mm} † is taken differing from the former investigation, where the boiling-point under the pressure of 28 Par. lin. is adopted. I have in the present instance preferred the metrical measure, in order to compare more easily my values with those calculated by M. Biot. Consequently, in the present case, the absolute expansion of the air from 0° — 100° or 100α is equal to the apparent expansion for the air contained in the thermometer from 0° — 100° C. 0·36394 resulted as the mean of several observations, whence we find $\delta = 0{\cdot}0000208$ ‡. In this manner the observations arranged in the following table were obtained, to which are appended the values calculated from the formula, which will be mentioned subsequently at p. 233.

* Poggendorff's *Annalen*, vol. lvii. p. 191.

† In strictness it ought to have been about 759·52^{mm}. See Professor Miller's Note at the end of this Memoir.—Ed.

‡ Poggendorff's *Annalen*, vol. lv. p. 17.

Numbers.	Temperatures.	Forces of expansion. Observed.	Forces of expansion. Calculated.	Difference.	Numbers.	Temperatures.	Forces of expansion. Observed.	Forces of expansion. Calculated.	Difference.
	°					°			
1	−6·61	2·75	2·75	0·00	56	+74·00	274·63	276·03	+1·40
2	−5·31	2·95	3·04	+0·09	57	74·08	275·60	276·96	+1·36
3	−3·64	3·45	3·45	0·00	58	74·13	276·53	277·55	+1·02
4	−0·99	4·15	4·21	+0·06	59	74·47	281·57	281·55	−0·02
5	−0·00	4·59	4·525	−0·065	*60	74·83	284·97	285·84	+0·87
6	.....	4·59	.....	−0·065	61	75·36	288·99	292·27	+3·28
7	.....	4·44	.....	+0·085	62	75·63	290·72	295·59	+4·87
8	.....	4·54	.....	−0·015	63	76·26	300·44	303·46	+3·02
9	.....	4·49	.....	+0·035	64	76·74	309·55	309·58	+0·03
10	.....	4·49	.....	+0·035	65	76·79	308·97	310·22	+1·25
11	.....	4·54	.....	−0·015	66	77·47	320·41	319·08	−1·33
*	Mean.	4·525			67	77·70	321·01	322·12	+1·11
12	+ 8·01	7·93	7·97	+0·04	68	78 33	330·13	330·58	+0·45
13	8·05	8·07	7·99	−0·08	69	78·72	332 01	335·91	+3·90
14	8·05	8·22	7·99	−0·23	70	81·77	379·54	380·17	+0·63
*15	11·34	9·43	9·97	+0·54	71	81·89	382·18	382·01	−0·17
16	11·36	9·38	9·99	+0·51	72	81·95	385·34	382·93	−2·41
17	11·93	9·88	10·37	+0·59	73	82·12	384·33	385·55	+1·22
*18	11·98	9·88	10·41	+0·53	74	82·12	385·85	385·55	−0·30
19	12·07	9·93	10·47	+0·54	*75	82·25	387·15	387·56	+0·41
20	12·72	9·88	10·61	+0·73	76	82·84	397·82	396·81	−1·01
21	12·31	10·28	10·64	+0·36	77	84·26	420·37	419·85	−0·52
22	13·06	10·48	11·17	+0·69	78	84·29	421·61	420·35	−1·26
23	13·10	10·58	11·20	+0·62	79	84·56	426·65	424·86	−1·79
24	16·82	13·52	14·24	+0·72	80	84·68	427·60	426·88	−0·72
25	23·30	21·80	21·29	−0·51	81	84·99	428·89	432·13	+3·24
26	23·43	21·82	21·38	−0·44	82	85·12	431·05	434·34	+3·29
27	23·83	22·93	21·99	−0·94	83	85·32	434·44	437·77	+3·33
*28	23·85	22·24	22·02	−0·22	84	85·91	444·69	448·02	+3·33
29	35·95	43·96	44·15	+0·19	85	86·21	450·64	453·31	+2·67
30	43·13	63·58	64·83	+1·25	86	86·23	450·54	453·67	+3·13
31	44·89	71·01	71·02	+0·01	87	86·29	449·90	454·73	+4·83
*32	44·90	71·20	71·06	−0·14	88	86·29	450·04	454·73	+4·69
33	45·26	71·90	72·39	+0·49	89	86·29	450·70	454·73	+4·03
34	45·46	73·14	73·13	−0·01	90	86·33	452·05	455·44	+3·39
*35	45·70	73·74	74·04	+0·30	91	88·79	504·27	501·00	−3·27
36	45·77	73·94	74·31	+0·37	92	89·05	506·96	506·03	−0·93
37	51·19	96·35	97·54	+1·19	93	89·64	518·07	517·61	−0·46
38	51·36	96·48	98·36	+1·88	*94	90·80	542·54	541·01	−1·53
39	52·12	101·40	102·12	+0·72	95	91·34	553·03	552·20	−0·83
40	54·16	110·16	112·73	+2·27	*96	91·81	563·50	562·10	−1·40
41	54·24	111·79	113·17	+1·18	97	93·57	601·56	600·51	−1·05
42	54·54	113·10	114·81	+1·71	98	93·66	601·08	602·53	+1·45
43	54·64	113·57	115·37	+1·80	99	93·66	601·78	602·53	+0·75
44	54·70	114·55	115·70	+1·15	100	97·85	708·50	703·15	−5·35
*45	54·74	114·65	115·92	+1·27	101	98·40	722·91	717·35	−5·56
46	54·80	115·15	116·26	+1·11	102	98·90	736·90	730·46	−6·44
47	54·83	115·35	116·42	+1·07	103	99·03	739·40	733·90	−5·50
48	55·39	118·61	119·59	+0·98	104	99·39	743·56	743·49	−0·07
49	55·39	118·86	119·59	+0·73	105	99·40	743·10	743·76	+0·66
50	55·56	118·93	120·57	+1·64	106	99·47	745·22	745·64	+0·42
51	58·19	135·45	136·55	+1·10	107	99·66	746·99	750·76	+3·77
52	58·68	139·13	139·72	+0·59	108	100·52	780·06	774·29	−5·77
53	72·59	258·28	260·00	+1·72	109	100·87	779·73	784·07	+4·34
54	72·95	265·34	264·02	−1·32	110	104·64	901·70	895·83	−5·87
55	+73·19	269·74	266·72	−3·02	111	+104·68	904·15	897·08	−7·07

It may appear surprising that the observations present such great variations; but if it be considered that 0°·1 C., at least with temperatures above 50° C., causes a difference in the expansive force of about 2^{mm}, it would scarcely be possible to expect greater accuracy. The readings of the air thermometer may indeed be obtained to within 0°·01 C., but the errors possible in these readings render such slight differences of temperature uncertain. Besides such errors dependent on the observation of the temperature, the method itself gives rise to the following. In the first place, the coincidence of the horizontal wire of a telescope with the meniscus of mercury is always uncertain on account of the reflexion, and then in the carrying of the telescope along the kathetometer its axis never remains perfectly parallel. This latter inconvenience I have rendered less great by always adjusting this telescope too high, and clamping it to the kathetometer, and then gradually lowering it by means of the micrometer screw until the line touched the mercurial trough; in fact, by always operating with the micrometer screw in the same direction in adjusting the telescope. With this precaution the sum of the errors of all the seven readings belonging to one observation did not amount at the utmost to $0{\cdot}15^{mm}$, within which limit all the experiments made at 0° come. Moreover, the observations might be rendered inaccurate from my want of success in depriving the water employed entirely of air, either by interrupted and long-continued boiling, or even by allowing it to ascend almost boiling hot through the mercury. Already Watt, and after him Southern, experienced the same difficulty *. No air was, it is true, visible at the ordinary temperature and pressure of the atmosphere, but when vapour had formed by the diminution of the pressure and increase of the temperature, an air bubble remained above the water after it had cooled, which however, under the pressure of the atmosphere, was only about $0{\cdot}5^{mm}$ in diameter. After some hours it had always disappeared and was absorbed by the water. When the experiment was again commenced the above-mentioned sudden evolution of steam usually happened.

Since the space which was occupied by the vapour in the tube *a b d* was never smaller in my experiments than 7 cub. cent., the air bubble occupied at 0°, and the pressure of one atmosphere at the furthermost 0·00001 of this space, the expan-

* Robison's System of Mechanical Philosophy, ii. p. 31 and 170.

sive force therefore of the steam could scarcely fall out 0·000014 too high from this cause, even at 105° C., the highest temperature employed.

The principal source of error however in these experiments is owing to its being impossible to expose the air thermometer and the vapour to absolutely the same temperature. It is on that account that the observations at 0°, which were made in melting ice, when consequently the temperature remained perfectly constant and no air thermometer was required, differ so little from one another.

If the observed values be compared with Dalton's older results, which were founded partly on the observation of the boiling-point under the receiver of the air-pump, and partly by direct measurement of the expansive forces, or with the table calculated by Biot from them, it will be seen that they differ from these in so far as the expansive forces observed by me for low temperatures are altogether smaller, as well as in those above 88° C., while in the central degrees they are larger.

Although the expansive force at 0° is supported by the coincidence of various observations, yet it differs considerably from the assertions of all earlier observers; and even although the expansive forces of the temperatures situated near 0° confirm the view that it must be lower than has hitherto been admitted, yet it is precisely this observation which is of such great importance for the establishment of a formula of interpolation, that it appeared to me desirable to test it likewise by another method. I therefore selected the former, as it had been executed by Gay-Lussac; but I soon became convinced how much in it depended on the consideration of the capillarity if accurate results were to be obtained.

A barometer tube was made use of which in its upper part was bent at a right angle, precisely as in Gay-Lussac's experiment, only that it was more than 0·5 inch wide at the height where the surface of the mercury fell, so that in this case no capillary depression could take place. After some well-boiled water had been let into the empty space the horizontal part of the tube was surrounded with ice, in order that all the water might distil over into it. The vertical portion of the space in which the vapours were was then likewise surrounded with ice (although this was superfluous), and then the height read off with a kathetometer. But here the difficulty of observing the

surface in the vessel was encountered. The various observations yielded some lower and some higher numbers than 4·525; they, however, in no case attained the previously adopted value, 5·06. The mean from them would be 4·62. I however give the preference to the number found by my method, $4{\cdot}525^{mm}$, because the single observations offer smaller differences.

In order to calculate the expansive forces for entire degrees of temperature from the found values, a formula of interpolation was requisite. If we were acquainted with a law of the dependency of the expansive force of the temperature and all the other quantities which necessarily come into consideration, we should be able to suggest a theoretical formula which would certainly be preferable to all others, but unfortunately up to the present nothing is known of this law. Roche has attempted to give such a theoretical formula, but the reporter of the French Commission* says of the considerations upon which it is based, that they are not deserving of the approbation of physicists. Recently Von Wrede† has likewise proposed a theoretical formula; but however ingenious its derivation, it still depends on some hypotheses which have not hitherto been sufficiently established; I therefore thought it right to content myself with a purely empirical formula, *i. e.* with such a one as represents with sufficient accuracy the results of the observations.

At present we already possess an immense number of formulæ for the same purpose. That none of these could suit my observations is evident, since their coefficients have been determined from other experiments; but it was interesting to ascertain what form of these different equations might probably correspond with them best.

Several examinations of the form of the equation suggested by Laplace and modified by Biot‡, which expresses the expansive forces by a series arranged according to ascending powers of the temperatures as well as of that proposed by Egen§, which expresses the temperatures by a series arranged according to ascending powers of the logarithm of the expansive force, have shown that these forms can only be made to agree with the observations when the whole of them are used for the determina-

* *Annales de Chimie*, xliii. p. 105.
† Poggendorff's *Annalen*, liii. p. 223.
‡ Biot, *Traité*, i. p. 273.
§ Poggendorff's *Annalen*, xxvii. p. 9.

tion of the coefficients. But the form which has been employed by the French academicians, by T. H. Young, Creighton, Southern, Tredgold and Coriolis, and also quite recently by the author of the article 'Steam' in the *Encyclopædia Britannica*, and in which the expansive force is equal to a power multiplied by a constant number of increased temperature, corresponds less well with them, whatever power be assumed, than the form proposed by Roche, August* and Strehlke, which is at the same time that to which theoretical considerations have led Von Wrede, and in which the expansive force is expressed by a constant number multiplied by another constant number raised to a power whose exponent contains the temperature in numerator and denominator, so that if e denote the expansive force of the vapour expressed in millimetres, and t the temperature in degrees of the centesimal scale, we have

$$e = a \cdot b^{\frac{t}{\gamma + t}}.$$

I have consequently chosen this form of the equation.

For $t = 0$ we have $e = a = 4{\cdot}525^{\text{mm}}$;

for $t = 100$ we have $e = 760^{\text{mm}} = 4{\cdot}525 \cdot b^{\frac{100}{\gamma + 100}}$.

This equation exhibits a relation between b and γ, and it now only remains to determine one of these two quantities from the observations. I have for this purpose selected the ten observations marked with a * in the table, p. 229, and from this γ is determined according to the method of least squares, whence resulted $\gamma = 234{\cdot}69$ and $\log b = 7{\cdot}4475$. We therefore obtain

$$e = 4^{\text{mm}}{\cdot}525 \cdot 10^{\frac{7{\cdot}4475\, t}{234{\cdot}69 + t}}.$$

For comparison, I have appended to the observations given in the table inserted at p. 229, the values of e calculated according to this formula. The following table contains the expansive forces for all integer degrees from -20 to $+118°$ C.

* Poggendorff's *Annalen*, vol. xiii. p. 122, and vol. lviii. p. 334.

Table of the Expansive Forces calculated according to the formula

$$e = 4^{\text{mm}}\cdot 525 \,.\, 10^{\frac{7\cdot 4475\, t}{234\cdot 69 + t}}.$$

t.	*e.*	*t.*	*e.*	*t.*	*e.*	*t.*	*e.*	*t.*	*e.*
°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.
−20	0·916	+8	7·964	36	44·268	64	178·397	92	566·147
−19	0·999	9	8·525	37	46·758	65	186·601	93	587·836
−18	1·089	10	9·126	38	49·368	66	195·124	94	610·217
−17	1·186	11	9·751	39	52·103	67	203·975	95	633·305
−16	1·290	12	10·421	40	54·969	68	213·166	96	657·120
−15	1·403	13	11·130	41	57·969	69	222·706	97	681·683
−14	1·525	14	11·882	42	61·109	70	232·606	98	707·000
−13	1·655	15	12·677	43	64·396	71	242·877	99	733·100
−12	1·796	16	13·519	44	67·833	72	253·530	100	760·000
−11	1·947	17	14·409	45	71·427	73	264·577	101	787·718
−10	2·109	18	15·351	46	75·185	74	276·029	102	816·273
− 9	2·284	19	16·345	47	79·111	75	287·898	103	845·683
− 8	2·471	20	17·396	48	83·212	76	300·193	104	875·971
− 7	2·671	21	18·505	49	87·494	77	312·934	105	907·157
− 6	2·886	22	19·675	50	91·965	78	326·127	106	939·260
− 5	3·115	23	20·909	51	96·630	79	339·786	107	972·296
− 4	3·361	24	22·211	52	101·497	80	353·926	108	1006·300
− 3	3·624	25	23·582	53	106·572	81	368·558	109	1041·278
− 2	3·905	26	25·026	54	111·864	82	383·697	110	1077·261
− 1	4·205	27	26·547	55	117·378	83	399·357	111	1114·268
0	4·525	28	28·148	56	123·124	84	415·552	112	1152·321
+ 1	4·867	29	29·832	57	129·109	85	432·295	113	1191·444
+ 2	5·231	30	31·602	58	135·341	86	449·603	114	1231·660
+ 3	5·619	31	33·464	59	141·829	87	467·489	115	1272·986
+ 4	6·032	32	35·419	60	148·579	88	485·970	116	1315·462
+ 5	6·471	33	37·473	61	155·603	89	505·060	117	1359·094
+ 6	6·939	34	39·630	62	162·908	90	524·775	118	1403·915
+ 7	7·436	35	41·893	63	170·502	91	545·133		

[For the following note (referred to at p. 228.) the Editor is indebted to Professor Miller of Cambridge, to whose revision the translation has been submitted.]

According to the definition of Laplace in the introduction to the *Exposition du Système du Monde*, 100° C. is the temperature of boiling water (supposed to be the same as that of the steam) under the pressure of 0·76 metre of mercury at 0° C. at the mean level of the sea in lat. 45°. Now they all assume the boiling-point to be the temperature of steam under the pressure of 0·76 metre of mercury at 0° C. at any place—Berlin or Paris. But on account of the variation of gravity, the pressures of 0·76 metre at those places are considerably different from that of 0·76 metre in lat. 45°; for instance, in lat. 51° 12′ the pressure of 0·759·52 metre of mercury is equal to the pressure of 0·760 in lat. 45°. The difference of half a millimetre, or about 0·02 inch, is a magnitude which these observers pretend not to neglect.

Article IX.

On the Force requisite for the production of Vapours. *By Prof.* Gustav Magnus*.

[From Poggendorff's *Annalen*, 1844. No. 2.]

I HAVE previously mentioned at page 226 that the water in the arm of the U-shaped tube *a b d* which had been well-boiled did not generally pass into the form of steam until it was under a pressure by several inches mercury lower than that which corresponded to the expansive force of the vapours at the temperature existing, but that then the formation of steam took place suddenly and with great violence. This phænomenon had, as I subsequently found, been already observed by Watt†, and after him by Southern, in precisely the same way in the barometer tubes which they employed in their experiments. But neither have they, nor has any one since, drawn any conclusion from this phænomenon.

Evidently the force necessary for the disengagement of the steam was greater than the expansive force of the steam at the existing temperature. If we were to admit that the formation of steam had been rendered difficult, owing to the attraction between glass and water, it cannot be conceived why in such case the parts of the water did not separate from each other, the more so as it was always present in such quantity and constantly occupied so large a space, that the attraction of the glass could not possibly have extended to its inner parts.

It therefore remains only to admit that the force which is required for the production of steam is larger than its expansive force, or the force which it requires for its existence, because the cohesion of the fluid upon which its liquid condition rests must be overcome.

It has already been asserted that the cohesion must be done away with in the formation of steam, but it has been regarded as very inconsiderable and has been neglected. On that account no one has deduced the conclusion from it, that the particle of liquid to be converted into vapour must constantly possess a

* Translated by W. Francis, Ph.D., F.L.S.

† Robison's System of Mechanical Philosophy, ii. pp. 31 and 170.

higher temperature than corresponds to the expansive force of the steam at the temperature existing.

When the liquid only evaporates it will not be possible to observe whether it has a higher temperature than the liberated steam, because the evaporation proceeds solely from the surface, and the deeper portion of the fluid may possess quite a different temperature. Nor even at the surface will the fluid be *much* warmer than the vapour, because there, where it is in contact with the air, its parts are not held back by exactly as great a force as in the interior, where every particle is surrounded on all sides with particles of the same nature. This is the reason why the above-mentioned phænomenon never occurred when a bubble of air, however small, was situated above the water.

On the contrary, during ebullition, when the formation of steam proceeds from the bottom of the vessel, the liquid will always be warmer than the evolved steam. This is most evident in boiling saline solutions: in these the cohesion between water and salt is greater than between the parts of the water among one another, and consequently a higher temperature is required to overcome this cohesion; moreover, the steam, as long as it is still in the saline solution, retains an expansive force corresponding to this high temperature, otherwise it would again become fluid by the attraction of the salt. This is already manifest from the fact, that on introducing a salt, for instance soda into the water contained in the vacuum of a barometer, its expansive force is immediately diminished*. But to prove this in a still more convincing manner, I introduced some water into the tube *a b d*, which was used for the production of the steam, and exposed it to a temperature of 100° C. The steam which had thus originated possessed an expansive force equal to the pressure of the atmosphere; but if I now conveyed into the water a solution of common salt, the expansive force of the steam decreased immediately by several inches of mercury.

In the same manner I passed the vapours of boiling water, which had a temperature of 100° C., into a solution of common salt, which was maintained at 100° C. on a water-bath. The result was that the solution of salt became heated to 107° C., although the heating body, viz. the aqueous vapours, were not hotter than 100° C.; but these were absorbed by the solution of salt and yielded their latent heat to this until they had attained

* Biot, *Traité de Physique*, i. p. 285.

a temperature at which the expansive force of the aqueous vapours sufficed to overcome the pressure of the atmosphere, and moreover, the cohesion between water and salt, that is the temperature at which the solution of salt boils. The solution gradually became diluted, and at the same time its temperature decreased; if more salt was then added, it again rose to the boiling-point corresponding to the new degree of concentration.

With pure water, or any other pure boiling liquid, it is quite different than with saline solutions. In them the particle to be converted into vapour must likewise possess so high a temperature that the expansive force of the vapours be not merely sufficient to overcome the pressure, but likewise the cohesion. The vapour formed at this higher temperature being no longer attracted by the water present, expands even within the liquid corresponding to the pressure under which it is; consequently the temperature of boiling water can never be so high as that of a solution of salt; nevertheless, however, boiling water has constantly a higher temperature than the steam which escapes, as was recently demonstrated experimentally by M. Marcet*.

That, however, it is generally but very little higher, is evident from the following:—When a liquid is boiled in a vessel the sides of which attract it more powerfully than its parts attract each other, these latter will separate more readily from one another than from the sides of the vessel. For this reason the liquid in such vessels cannot assume any higher temperature than that at which the expansive force of the vapour suffices to overcome the pressure and the cohesion of the liquid. This temperature is the highest which the liquid can acquire under the pressure existing, and it would indicate this if it could be boiled in vessels formed as it were of the same liquid, or, as already stated, in vessels the sides of which retain it *everywhere* more powerfully than the parts attract each other. If, on the contrary, it is boiled in a vessel whose sides hold it back with less force than its homogeneous parts, only a less force will be requisite to separate it from these sides than from its homogeneous parts, and consequently the formation of steam will result in this case more easily. Consequently the boiling-point is so much the lower the weaker the attraction of the sides or any body presents for the liquid. This may, therefore, really be lowered by the sides of the vessel, but never raised, at least not above the tempera-

* Poggendorff's *Annalen*, vol. lvii. p. 218.

ture at which the liquid would boil without the presence of a foreign body. We should, however, be led to imagine that a smooth metallic surface, because it attracts the water more powerfully than the parts of the water attract one another, would not lower but raise the boiling-point, while experience teaches the contrary. But if a metallic surface, even when it has been most completely cleansed, be immersed in water, it adheres in general; but there are always some places where it does not adhere, and from which it withdraws itself, where therefore the attraction to the water is smaller than that existing between the parts of the water. The same is the case with glass, only when this has been purified by boiling in sulphuric or nitric acid does the water form a continuous coating, otherwise there are always found some spots where it does not adhere. Consequently the boiling-point, even in glass vessels which have been purified in the above manner, is, as was shown by M. Marcet, frequently 5° C. higher than the temperature of the liberated vapour; and probably this is likewise the temperature at which the water would boil without the presence of a foreign body. On repeating this experiment I did not find the boiling-point 5° C., which, as stated by Marcet, is not always readily attained, but yet several degrees higher than the temperature of the evolved steam. I have, moreover, attempted to clean a platinum dish by fusing caustic potash and then by sulphuric acid, and in this manner I have equally succeeded in raising the boiling-point of the water, but not so considerably as with glass. This, probably, is owing to my platinum vessel having been already frequently employed and not being free from scratches, &c., which in this instance acted like pulverulent bodies; for these, as is well known, lower the boiling-point most, so that by the introduction of powdered glass or metal into boiling water, its temperature can scarcely be distinguished from that of the escaping steam.

If, moreover, we bear in mind that towards each particle of dust which may fall in, the adhesion of the water is smaller than the cohesion of its parts, and that the adhesion of solid bodies is modified by the most varied circumstances, so that as recent discoveries show, light, heat, electricity, nay, even the mere vicinity of another substance, modify the surface of a body to such an extent that the vapours of water and mercury deposit themselves at various places differently, it cannot be surprising if the presence of metal or glass did not, except in some rare instances,

lower the boiling-point of the liquid. This lowering, and consequently the temperature of the boiling-point, varies not merely according to the different nature of the vessel and its purity, but even every particle of dust that falls into the liquid alters the relation of adhesion, and consequently the boiling-point. But if the liquid be protected against dust, and the bodies present be preserved from every change, the boiling-point, nevertheless, varies constantly; for as soon as the temperature is sufficiently high to overcome the cohesion at any one place and form vapour, this expands even in the liquid, and from its assuming here the expansion and temperature corresponding to the pressure, it cools the liquid. If this boil at a temperature several degrees higher than that of the escaping vapour, the expansion of these latter will be considerable, and the cooling of the liquid produced each time correspond to this expansion, upon which a considerable time elapses until its temperature is sufficiently high to overcome the cohesion. It is on this account that a sensitive thermometer constantly changes in such a boiling liquid, and the evolution of the vapour is always connected with a kind of thumping. If, on the contrary, the boiling-point has been rendered by the presence of pulverulent substances or wires but slightly higher than the temperature of the escaping vapour, a very inconsiderable expansion of the vapour occurs, and while the boiling-point remains nearly constant, every sudden boiling up and thumping is avoided.

There does not exist an older physical experiment, nor one more frequently repeated than that of boiling water; but nevertheless, what occurs in the process was not sufficiently known, and even now much still remains unexplained.

Article X.

On the Allotropy of Elementary Bodies as one of the causes of the Isomerism of their Compounds. By* J. J. Berzelius.

[*Vetensk. Akad. Handling.* f. 1842. Poggendorff's *Annalen*, 1844.]

In the annual report on the progress of chemistry, presented to the Royal Academy of Stockholm in March 1840, I have proposed to designate by the term *allotropic state*, that dissimilar condition which is observed in certain elements, and long-known examples of which are found in the different forms of carbon, as graphite and diamond. I there endeavoured at the same time to show, that what we in compound bodies call isomeric modifications, in certain cases depend upon the circumstance that the elements contained in one of these compounds exist in a different allotropic state from that in the other, whilst in other cases the isomerism distinctly depends on the atoms of the simple elements being combined in a different order, various examples of which I also brought forward, which it would be superfluous to enumerate in the present instance.

Although these dissimilar conditions, which I have here called allotropic, have long since attracted attention in one or two elements, still they have been regarded as exceptions to the general rule. It is at present my object to show that they are not so rare, that it is probably rather a general property of the elements to appear in different allotropic conditions, and that, although we have hitherto been unable to obtain several of the elements when uncombined in their allotropic states, still their compounds indicate the same with tolerable distinctness.

Since the discovery that the diamond, like graphite and charcoal, combines with oxygen to form carbonic acid, we are convinced that the ponderable material in them is one and the same element, notwithstanding the remarkable differences in their combustibility, their specific gravity, specific heat, and their behaviour to light and electricity. So long as this was not known in the case of other bodies it was regarded as an exception. We

* From the German by J. W. Griffith, M.D.

subsequently became acquainted with dissimilar conditions of the same kind in silicium, phosphorus, and finally (as Frankenheim proved in 1839 by ingenious experiments*) in sulphur. To express these dissimilar conditions in writing, he proposed annexing the letters α, β, γ to the symbols of the elements. Although Frankenheim made no distinction between the isomerism of compound bodies and the dissimilarity of the condition of the elements which he included under the same name, isomerism, still the first clear notion of it is put forth in the researches we have mentioned. I shall endeavour to extend this a little further, and I now pass on to the consideration of the relation of the different elements according to this view.

Carbon appears to occur in three different allotropic states, viz. as—

1. *Charcoal*, which I shall distinguish by C_α. It is characterized by its ready inflammability, its property of being completely consumed in the air at the temperature generated by its combustion, and lastly by its greater specific heat, which amounts to 0·24. It may justly be urged against the view that charcoal is an allotropic modification of the element carbon, that it usually contains hydrogen. However, that this does not amount to more than what may be regarded as accidental, arising from the mode of its preparation, is evident from the fact that it can be expelled, either by heating it to low redness in a current of chlorine, or by retaining it at a low red heat exposed to the air, without its being converted into the next modification, which however is effected by exposing it for some time to an intense red heat. There is still another method by which the carbon may be transformed into this allotropic condition, that is, by decomposing carbonate of potash or soda with potassium at a gentle heat, dissolving the saline mass in water and washing out the carbon. This carbon is still more combustible than charcoal, and burns still more vividly than the latter when in the form of powder.

2. *Graphite*, C_β, with its well-known varieties, anthracite, coke, fossil coal, &c.

3. *Diamond*, C_γ.—Both these are characterized by their difficulty of combustion. The diamond crystallizes in forms of the regular cubic system, is colourless, transparent, and almost the hardest body known. Graphite is obtained in a crystalline state

* *Journ. für Prakt. Chemie*, vol. xvi. p. 1.

very rarely in the mineral kingdom, but more frequently by art. Its crystalline form has not been accurately ascertained; but so far is certain, that it cannot be referred to the forms assumed by the diamond. The carbon in these two modifications is thus dimorphous. Graphite has a metallic lustre, is dark gray and transparent. The specific gravity of the diamond is 3·5, that of graphite barely amounts to 2·5. The specific heat of the diamond is 0·147, that of graphite from 0·197 to 0·20. Two different elements could scarcely differ more than these allotropic modifications of one and the same element; the diamond is a non-conductor of electricity; graphite and coke are good conductors.

The allotropic states of carbon are thus remarkably distinct in their different specific gravity and specific heat (which seem to depend on one another), in their crystalline form and their ready combustion with oxygen.

I will here observe, that in like manner as we are acquainted with carbon in the condition C_α, and nevertheless find it impossible to transform into it carbon of either of the other two conditions, this may also be the case with regard to other elements, *i. e.* allotropic conditions of them may exist, into which we cannot bring them.

We know not whether the allotropic conditions of the carbon in the majority of compounds, especially organic, into which it enters, and among which so many isomeric forms occur, influence in any way the difference of their properties; when, however, we compare the chemical properties of carbonic acid with those of oxalic acid, we are led to suppose that they contribute to it.

Silicium most resembles carbon as regards its first two allotropic states.

Si_α is produced when the silicium is obtained by reduction with potassium. It takes fire and burns vividly at a slightly elevated temperature; it detonates when thrown on nitre in a state of fusion; it evolves heat, and is volatilized with hydrofluoric acid; combines with sulphur when gently heated with it, and the resulting compound is decomposed by water, sulphuretted hydrogen being evolved and silicic acid formed, which last is soluble in water, and still more so in hydrochloric acid.

Si_β is formed when the preceding modification is exposed to a strong red heat; the silicium, however, requires a far less in-

tense heat than carbon to effect this transformation. It may now be subjected to a white heat before the flame of a blowpipe without inflaming; it may be fused with nitre, even at an incipient red heat, without producing decomposition; fluoric acid has no action upon it; and it cannot be made to enter into combination with sulphur.

Silicium likewise yields a number of isomeric compounds, but it is far more evident than in the case of carbon what share its allotropic state has in their different nature. We have remarked that Si_α, combined with sulphur, yields a form of silicic acid which is soluble in hydrochloric acid and even in water. Consequently it is tolerably clear that the isomeric modification of silicic acid soluble in hydrochloric acid has Si_α for its radical. On the other hand, although it cannot be proved by direct experiment, it is pretty evident that quartz, rock crystal, and the artificially prepared insoluble silicic acid, contain the radical Si_β, the original properties of which are evident in its compounds.

The mineral kingdom furnishes a number of silicates which are entirely soluble in hydrochloric acid. When these are dissolved, one of two things happens; either the acid extracts the bases, leaving the silica, or the bases remain insoluble in the acid. It has been attempted to attribute the solubility of these silicates to the water which they ordinarily contain chemically combined; but the water has nothing to do with it, as is evident from the fact that garnet and idiocrase, as they occur in the mineral kingdom, are perfectly insoluble in hydrochloric acid, and only become so when they have been fused into a glass, whereby their specific gravity is perceptibly diminished. It is thus evident that the water they contain proves nothing further than that the compound was never exposed to those influences which induce the production of the insoluble modification, when at the same time the water would have been expelled. In addition to these the mineral kingdom yields silicates upon which neither acids, nor fusion with bisulphate of potash at a red heat, exert any decomposing influence. Glass, which is artificially produced, is another example. That the radical of the silicic acid in them is Si_β is highly probable; but it is not easy to imagine why such bases as potash, soda, lime, &c. should assume the same indifferent state towards the acid. We shall subsequently return to this point.

The experiments of Frankenheim, which I have already al-

luded to, satisfactorily prove that *sulphur* is capable of assuming three allotropic states. Scheerer and Marchand have shown that S_α and S_β possess peculiar crystalline forms with different specific heat and gravity. Frankenheim demonstrated that S_γ possesses a still lower specific heat than either of the others, and proved that the abnormal specific gravity of the vapour of sulphur arises from its having been evolved from S_γ. We know, however, that the vapour of sulphur in sulphurous acid and sulphuretted hydrogen, which probably contain S_α, possesses its normal specific gravity.

It is not altogether improbable that these different allotropic conditions of the sulphur exist in the various classes of its acids.

Phosphorus, also, in all probability, has three allotropic states, two of which may be traced in the different compounds of phosphorus, by a method which I think I have shown in my treatise on the combinations of phosphorus with sulphur *. The possibility, in this case, of tracing its relations accurately, laid the foundation for extending the same views to other elementary bodies.

Selenium resembles sulphur; it exists in a soft uncrystalline state, when it may be drawn into threads, representing S_γ. In its steel-gray crystalline and its beautiful red state, in which it is precipitated from its gaseous form upon cold bodies, or in the moist way by sulphurous acid, phosphorous acid, zinc, &c., it may represent, the former S_α, and the latter S_β; but we have hitherto been unable to detect any combination of selenium which appears to belong to either allotropic condition more than the other.

We are acquainted with two allotropic conditions of *arsenic*. One, As_α, is produced when arsenic existing in the gaseous state with another gas which is heated, condenses upon the cool part of the subliming apparatus. It is of a dark gray colour, crystallizes, and becomes oxidized by exposure to the air, especially at a temperature of about 104° F., when it then crumbles to a black suboxide. The other form, As_β, is formed when arsenic is strongly heated or sublimed in a vessel, in which that part on which the sublimate is deposited is retained at about the temperature at which arsenic assumes the state of vapour. It is then deposited from an atmosphere of arsenic vapour. It is nearly

* *Kongl. Vet. Akad. Handl.*, f. 1842, p. 87. Poggendorff's *Annalen*, vol. lix. pp. 76, 463 and 539.

white, of a high metallic lustre, has a greater specific gravity than the preceding, and is not changed by the air, when in the finest powder, even at a temperature of 158° to 176° F., and sometimes even considerably above 212°.

Arsenious acid assumes both the corresponding isomeric modifications, and what is remarkable, they are formed by sublimation under exactly the same circumstances as the allotropic states of the metal. The radical of the vitreous acid is then As_{β}, and that of the white, or that which crystallizes in octahedrons, As_{α}. The higher specific gravity of As_{β} occurs likewise in the vitreous acid.

One isomeric modification only of arsenic acid is known to us; as far as we can conclude, from analogy with phosphoric acid, As_{α} is the radical in it.

Tellurium is also as yet known in but one allotropic modification, and even in that it has been but little examined. However, both tellurous as well as telluric acid possess two distinct isomeric modifications, and these are of such kind as lead us to presuppose allotropic modifications similar to those of silicium.

Exactly the same holds good with respect to *antimony*.

Chromium however affords a particularly instructive example. When oxide of chromium is reduced by charcoal at a very high temperature, it yields a pale gray metal, which cannot be oxidized either by a red heat or boiling with nitromuriatic acid. The action of fluoric acid, or combustion with potash or soda with access of air, or with nitre, are the only means whereby it can be brought to its original condition, which may be expressed by Cr_{β}.

When, on the contrary, chloride of chromium, free from water and oxide, is reduced by potassium, a gray pulverulent metal is likewise formed, which cannot be oxidized by boiling water, but when heated to between 392° and 572° F., inflames and burns vividly into the green oxide of chromium, and dissolves in hydrochloric acid with copious evolution of gas. This then is Cr_{α}.

We have here then the same behaviour as in the case of silicium, and the behaviour of oxide of chromium exactly agrees with that of silicic acid. We have a green oxide of chromium, which is soluble in acids, and, like the soluble silicic acid, at a higher temperature passes into the insoluble modification, resembling silicic acid which has been heated to redness; but in this transformation a vivid evolution of light occurs, which has never been

observed with the latter, and which characterizes this transition in several other bodies. When this modification of the oxide of chromium is crystallized, it scratches glass like crystallized silicic acid. It occurs in combinations, not only with sulphuric acid but also with several bases, and all these exhibit the same indifference towards reagents in the moist way, both Cr_β as well as the oxide which has been heated to redness. We are acquainted moreover with compounds of Cr_β with other bodies besides oxygen. H. Rose has shown that the chloride of chromium may be obtained in both conditions in the solid state. The aspect is the same; but one is readily soluble in water, and readily decomposed by reagents, whilst the other is insoluble and resists the action of reagents at a low temperature. We have thus evidently a chloride of Cr_α, and one of Cr_β.

But the oxide of chromium, in addition to the two isomeric states we have mentioned, assumes a third, viz. that in which it yields a blue hydrate, and red or violet salts with acids, from which, in the moist way, it passes into the state of green oxide, which yields green salts at a temperature even lower than 212° F. When its solution is concentrated, it passes in the course of time from green to red. Does this depend upon the existence of a third hitherto unknown allotropic condition of chromium, or upon other circumstances?

We have no ground for supposing chromium to exist in the state of Cr_β, either in chromic acid or in any of its compounds with bases with which we have hitherto become acquainted.

Titanium exhibits exactly the same phænomena as chromium. The stability of the red crystalline titanic acid, formed at a high temperature, both by a red heat and the action of nitromuriatic acid, is well known. But titanium, reduced at a low temperature from chloride of titanium by ammonia, by the method which H. Rose discovered, readily takes fire when heated, and burns vividly into titanic acid, is oxidized on being boiled with concentrated nitric acid, and is dissolved by nitromuriatic acid.

Titanic acid has its two corresponding isomeric modifications, and, like oxide of chromium, passes from the soluble into the insoluble state with evolution of light.

Tantalum, when reduced by potash and charcoal, does not exhibit any differences in its properties which allow of our supposing with any degree of certainty that it exists in several allotropic conditions. That which has been reduced by charcoal

at a high temperature certainly requires a high temperature for its inflammation, and a continued external application of heat to support its combustion, whilst that reduced by potassium, when heated to a certain point, quickly burns into tantalic acid; but these differences may depend on mechanical causes.

However, both tantalic acid and chloride of tantalum, according to Wöhler's experiments, have isomeric conditions, which correspond exactly with those of oxide of chromium and titanic acid, and allow of the supposition that the radical possesses corresponding allotropic modifications.

Uranium, reduced from the chloride by potassium, is one of the most combustible of the elementary bodies; it dissolves in diluted acids with violence, hydrogen being evolved. If we compare this condition with that which Richter ascribes to the regulus which he reduced from the oxide of uranium by heating it with dried and powdered ox-blood in a forge for an hour and a half, which certainly was not pure uranium, but still consisted principally of it, dissolved completely in nitromuriatic acid, but was scarcely affected by hydrochloric acid, we have the counterpart in allotropic state of the two isomeric modifications of the soluble and insoluble protoxide of uranium.

As regards the *soft* metals, it is more difficult to point out corresponding relations; however, there are some which deserve attention.

Tin, which in many points resembles titanium, has an oxide, which is isomorphous with titanic acid, and occurs in exactly the same two isomeric modifications. If we suppose these, in titanic acid, to depend upon dissimilar allotropic conditions of the radical, the same must also be the case with oxide of tin, or, as it is usually called, stannic acid.

Iridium and *osmium*, when artificially reduced, cannot be obtained of that high specific gravity which they possess when occurring in the mineral kingdom, nor in that state of indifference to reagents, which exists to such an extent that they cannot be made to combine with other metals in a state of fusion at a white heat, but separate with their continuity and form unaltered when the metal is dissolved. We can no more convert them artificially into this allotropic condition than we can transform charcoal into diamond.

But osmium, in the form in which we obtain it in the laboratory, burns readily on the application of heat, forming a volatile

oxide. Moreover, osmium forms lower oxides than the latter. These are reduced by hydrogen without heat, whereby the volatile oxide can be sublimed unchanged in hydrogen, and is only reduced when the mixture of the two gases is passed through a tube heated to redness. This is in opposition to what ordinarily takes place. The higher oxides are usually more readily reduced by hydrogen than the lower; here it is the reverse. Can this be satisfactorily explained by assuming that the osmium in the volatile oxide exists in a different allotropic condition to that in the lower degree of oxidation? I will moreover observe, that when osmic acid is reduced, by sulphurous acid for instance, its lower oxide is not produced, but a blue soluble one, which is in a still lower state of oxidation and quite distinct.

Iridium, when reduced in the moist way by formic acid, is soluble in nitromuriatic acid, according to Dobereiner. That reduced in a dry way, although equally pulverulent, is insoluble in it. As it occurs in the mineral kingdom, combined with one-fifth of platinum, it has the same specific gravity as platinum; but when obtained artificially, its specific gravity is seldom so great as 16·0. Experiments on the specific heat of bodies have led to the result, that their atomic weight multiplied by their specific heat gives similar products for all; consequently, if the atomic weight is the same, the specific heat must also be the same. In these experiments no regard was had to the different allotropic states, because they were then unknown; but with carbon this failed, as each modification had a different specific heat. This exception occurs also in iridium. Platinum and iridium have the same atomic weight; they must consequently possess also the same specific heat. But platinum, the specific weight of which is 22·55, according to Regnault has a specific heat of ·03243, which nearly agrees with Dulong and Petit's experiments; while iridium reduced artificially, of rather less specific weight than 16·0, possessed a specific heat of ·03683, thus full a seventh more. This iridium differs from that naturally occurring by characters which indicate two distinct allotropic states; and if we add to this what has just been mentioned, that iridium is soluble in nitromuriatic acid, it would indeed appear that iridium exists in three allotropic states; moreover, in the study of its combinations differences are perceptible in its properties, which serve clearly to indicate that iridium exists in them under three different allotropic conditions.

But what holds good with respect to iridium, may be imagined to be the case from analogy with platinum, rhodium and palladium, although hitherto experimental proof is wanting.

If the properties of the remaining metals are examined, we find here and there traces of analogous phænomena; but they have been so little followed out by experiment, that no positive conclusion regarding their existence can be drawn. I shall mention some of them.

Copper, when reduced by hydrogen at a heat below that of redness, on exposure to air soon becomes converted throughout its mass into protoxide; and when it is triturated for some time with an equivalent quantity of sulphur, it combines with it, according to Böttcher's experiment, producing flame and forming sulphuret of copper. If, however, the copper be reduced by hydrogen at a red heat, still considerably below the temperature at which it softens and begins to melt, it remains for years unchanged by exposure to air, and cannot be made to combine with sulphur without the application of heat*. Iron, cobalt and nickel, when reduced by hydrogen below a red heat, inflame after they have cooled if exposed to the air, and if they are immediately placed in water to avoid their taking fire, they inflame when they are again removed and have become nearly dry. If we compare this behaviour with that of iron reduced by heat, and with iron in that state in which it forms the conductor of a galvanic current without becoming oxidized, it would certainly appear that these peculiarities depended upon something more than a difference of mechanical condition.

When phosphate of iron is reduced by charcoal in a testing crucible, a regulus of phosphuret of iron is obtained. Both of its constituents have great affinity for oxygen, and the products of the combination with oxygen have a remarkable tendency to combine anew. But nevertheless this compound (the phosphuret of iron) is oxidized with great difficulty by heat, and is not in the least affected by dilute acids, and in order to dissolve it by nitric acid this must be very concentrated, and the phosphuret of iron must be finely powdered and boiled with it for a considerable time. Neither the properties of the phosphorus nor of the iron

* I take this opportunity of referring to the condition which copper assumes at a low red heat in a continuous stream of ammoniacal gas. On cooling it is pale gray, excessively brittle, and of a granular aspect. This certainly appears like a peculiar allotropic condition.

are here evident. The cause of the alteration cannot be in their combination, because their tendency to remain combined in the oxidized state, judging from their ordinary behaviour, must rather increase their affinity for oxygen; it must depend upon some other cause; and we can hardly imagine this to be any other than a different allotropic condition, similar to that which we have distinguished in silicium, chromium and titanium as β. If this conclusion be correct, it follows that this allotropic condition, even although it cannot be demonstrated by art in our experiments on the isolated elements, may still be proved to exist in their compounds.

Manganese, as we know, after reduction by charcoal in the forge, possesses the property of becoming oxidized without the application of heat, both in the air and in water, hydrogen being at the same time evolved. But Sefstrom has made the remarkable discovery, that when it is reduced by silicic acid, so that a compound containing 6·8 per cent. of silicium is obtained, a regulus is formed, which does not differ in appearance from the common one, but is not only deficient in the above-mentioned properties, but also may be retained at a red heat without becoming oxidized, and is not acted upon by nitromuriatic acid. With this great proportion of manganese, this want of affinity for oxygen cannot be attributed to the mechanical cause, that a covering of silicic acid is formed, which protects that part lying beneath it; for platinum, which contains a large amount of silicium, is readily soluble in nitromuriatic acid. The cause depends upon the altered properties of the substance; and it appears that silicium, in the state of $Si\beta$, has the power of converting the manganese into the condition $Mn\beta$, and this at a temperature at which the manganese itself retains its original allotropic condition.

If however this occurs with manganese in the reguline state, it must have a corresponding protoxide, the radical of which is $Mn\beta$, and the silicic acid, with the radical $Si\beta$, must also change the protoxide of manganese into this condition, and consequently produce a totally distinct silicate of manganese. Thus a new light is thrown upon the nature of the native red silicate of manganese ($\dot{\dot{M}}n^3 \dddot{S}i^2$), which is unaffected by the strongest acids, even when nitric acid forms the oxidizing agent.

It must not be overlooked, that what is possible with one metal, which constitutes one of the most highly positive known,

may also occur with one equally as strong or more strongly positive; and we then have an explanation of the fact, that many silicates of powerful bases, as alkalies and alkaline earths, protoxide of manganese or iron, &c., are perfectly indifferent towards the strongest reagents in the moist way.

It would then follow, that all elements are able to assume an allotropic condition corresponding to that here brought forward, and which we recognise with certainty in C_β, Si , Cr_β, and Ti_β; and that, although we cannot transpose an isolated element into this condition, yet it can be done when it is united with another element, if the last can be more readily brought, when the proper conditions occur, into the state distinguished as β.

We can thus understand why the compounds of antimonic, titanic, tantalic, silicic, and many other acids, so readily part with their bases, whilst not even a trace of them can be removed when the compound has been made to assume the other state by being heated to redness, because the transition of the radical of the acid into the state β has caused the same transition in the radical of the base.

If we glance over the extensive range of the compound inorganic bodies with which we are acquainted, we find abundant examples of combinations between elements of a dissimilar kind, which appear to belong to that condition of the radical which we have here called β, and which prove that the majority of the known elements may assume this state. Thus, for instance, the indifferent chloride of chromium shows that the halogens may participate in this condition.

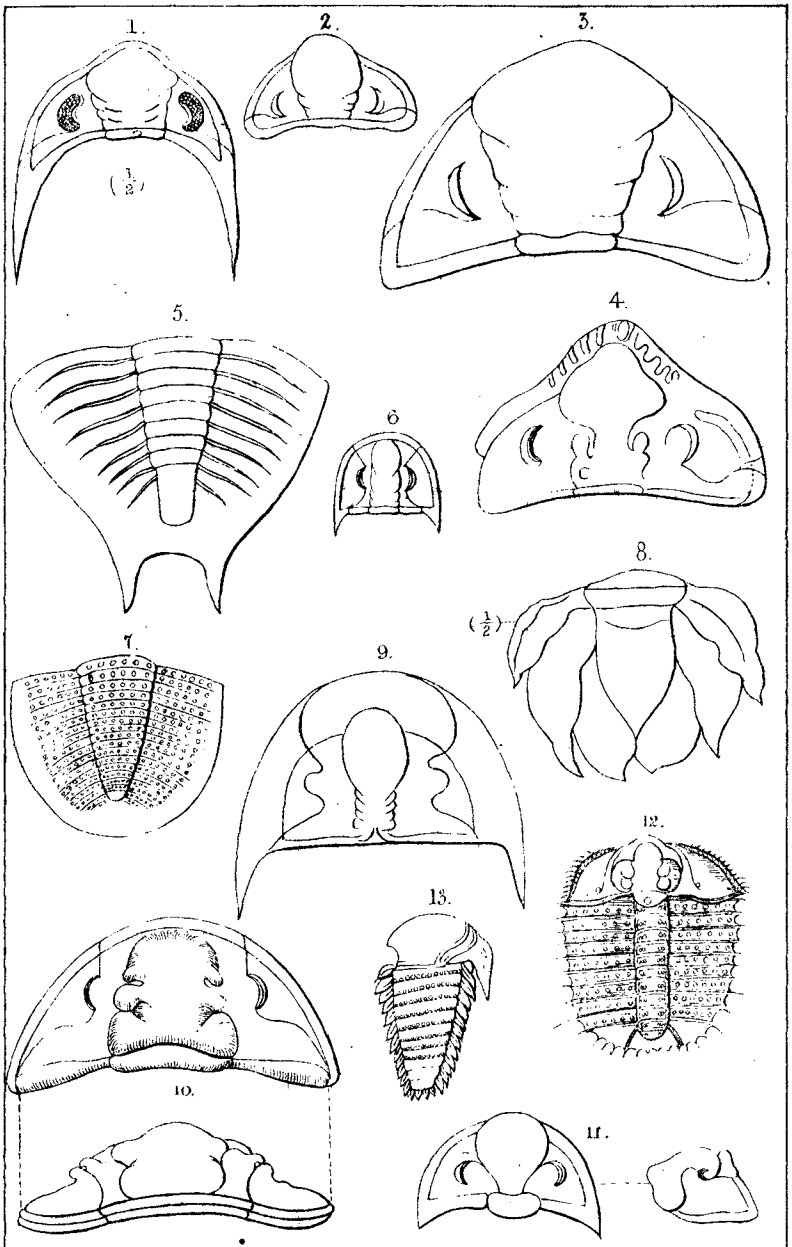
The difficulty of combustion of carburet of nitrogen may arise from the carbon existing in the state of C_β. But the difficult combustibility of phosphuret of nitrogen cannot be otherwise explained than by assuming that the phosphorus in it exists in the same indifferent state as in the phosphuret of iron, which we have distinguished as β. If we go further, we may suppose that the perfect indifference of carbon to form compounds depends upon its always existing in this state, and that when it combines with oxygen or hydrogen, circumstances must alter its state.

Among other bodies, the compounds of boron and nitrogen, lately discovered by Balmain*, are worthy of notice in this

* They are described in a paper read before the Chemical Society, Dec. 6, 1842, and published in the Philosophical Magazine, vol. xxii. p. 467.—Ed.

respect. Even compounds of potassium are insoluble in water, acids, and nitromuriatic acid; are not oxidized by being heated to redness in dry air, and are unaltered by a low red heat in a current of dry chlorine.

The facts I have adduced certainly still offer a rich field for speculations; yet the views advocated by me are not entirely without foundation. The subject deserves consideration, and if other inquirers give their attention to it, what is erroneous in the views I have brought forward will be separated, while at the same time that which is well-founded will be considerably extended.



1. Phacops Hausmanni Brgn.
2. Ph. Downingiae Murch.
3. Ph. Proavius m.
4. Odontocephalus Green.
5. Ph. Selenurus Green.
6. Phillipsia aequalis v.M.
7. Phillipsia ornata Portl.
8. Nuttainia hibernica Portl.
9. Oggyia dilatata Brünn.
10. Calymene Blumenbachii Brgn.
11. Griffithides globiceps Phill.
12. Odontopleura bispinosa m.
13. Remopleurides Kolbii Portl.

Article XI.

On the Morphology, Classification and Distribution of the Trilobites. By Dr. Emmerich *of Meiningen**.

[From Leonhard and Bronn's *Neues Jahrbuch für Mineralogie, Geologie und Petrefaktenkunde*, 1845, Part I.]

I. *Morphology of the Trilobites.*

Since the first scientific researches of Wahlenberg no further serious contest has arisen with regard to the arranging of the Trilobites among the Crustacea. As Crustacea they possess a body divided by transversal articulation into several successive rings, which, with the exception only of the genus *Olenus*, Zenk., and of the doubtful genus *Battus*, are of a threefold kind, viz. the anterior rings are united, as in *Limulus*, into a large cephalic shield, of the size of the whole width of the body, the shield bearing the organs of feeling and of mastication. The central rings are freely moveable and form the thorax, which always possessed six or more feet on its under side, corresponding to the number of joints: the posterior rings are likewise united with one another into a larger or smaller caudal shield, on which was situated the anus. Thorax and abdomen correspond with the thorax and abdomen of the *Isopoda* (wood-lice). The genus *Olenus*, already mentioned, is the only one which has homologous rings behind the head; so that there is between it and the other Crustacea a relation similar to that which exists between the Myriapoda (*Scolopendra* and *Iulus*) and the Spiders.

It is well known, that besides this tripartite division of the body into head, thorax and abdomen, there also exists a longitudinal division, separating the body into a central part and into the two sides. If we first consider the rings of the thorax, we find the two lateral portions, which adjoin the axis, to be free appendages, connected with the axis by perfect or imperfect articulation: these are the so-termed *fins*. These fins are hollow, adapted for the reception of muscles. Each of them probably corresponds with the two parts, which, in the rings of living Articulata, are designated *pleuræ*; with however the following distinction. Whilst in the latter they form part of the boundary of the cavity of the body of the animal, they are entirely ex-

* The Editor is indebted to the kind assistance of Prof. J. Phillips for the revision of this Article.

cluded from it in all the Trilobites, and constitute a free appendage, generally capable of a more or less independent movement. The cavity of the body, which contained the intestines of the animal, was only formed by the dorsal parts of the rings (*terga*), and by the abdominal parts opposite to them. The terga only have been preserved of these two different parts, owing to their having been of a calcareous nature in the living animals (Professor Hünefeld has found a considerable quantity of phosphate of lime, in addition to the carbonate of lime, in pieces of the shell); the abdominal portions were of a membranous nature, and decay has therefore destroyed them, together with the branchial feet, which were probably peculiar to these animals. Thus every ring consisted essentially of six elements. The structure of the rings of the tail entirely corresponds with this, with the exception that the free motion of the fins ceases simultaneously with the loss of the moveability of the joints of the axis, and that the former cohere immoveably among themselves and with the axis. The abdominal pieces were likewise of a membranous nature, and have therefore disappeared. The elements of the rings, by the junction of which the cephalic shield is formed, can also be demonstrated in the latter, in the same number and position as in the rings of the thorax; they bear the same relation to the latter as the elements of the dorsal vertebræ of Mammalia to those of the three vertebræ of the head; they are horizontally extended, and not united with one another by articulations but by sutures. These sutures remain distinctly visible in the Trilobites, forming a characteristic feature of the family. One of these sutures is very well known under the name of facial suture: for a long time it could not be explained by geologists, and has frequently given rise to strange interpretations (Pander), but much of its enigmatical character disappears on more accurate observation. These sutures, in my opinion, form an important objection against the ingenious hypothesis of Burmeister, who considers the *Battus* to be the most imperfect or undeveloped state of the Trilobites. *Battus* exhibits no traces of facial sutures. This assumption however is in opposition to a general law of nature, namely, that parts which were separated in the early state of an animal (for instance, the parts of the subsequently monopetalous flower, parts of the skeleton, as the pelvis, temple bone, &c.) may subsequently unite into one whole, but on the contrary a previously developed

whole can never be divided into various parts with increasing age. Such a division only takes place in the lowest stages of organic formation in the filaments of Confervæ, Worms and Radiata. It certainly is possible that this law may have but only *apparently* experienced an exception owing to the process of shedding the skin, to which the Trilobites were subject like all other Articulata. The circumstance that we meet with no differences in the shape of *Battus*, although all developed Trilobites are of so various a shape, is certainly a still more striking reason against that assumption; *Battus pisiformis* being almost the only definite species of the genus.

From the very first attempt at a separation of the Trilobites into genera, the compound eyes, in which respect they likewise correspond with all the living Crustacea, have been considered as particularly important. It is principally an alleged absence of them in many Trilobites, upon which particular stress has been laid, so much so, that even the cautious Dalman divided the genuine Trilobites into the two divisions of blind Trilobites and of those furnished with eyes; Brongniart indeed had to a certain extent already preceded him in this, and many others have followed the example. How far this deficiency of eyes can be scientifically demonstrated with respect to the genera *Ogygia*, *Paradoxides*, Brongn., *Conocephalus* and *Ellipsocephalus*, Zenk., will be seen from a more accurate investigation of the eyes in the *Calymenæ* and *Asaphi* of Brongniart, which according to general opinion were possessed of the faculty of vision. We find numerous species in both genera, in which even the naked eye can detect the same structure as in many recent genera, but scarcely anywhere so beautiful in the latter, nor formed on so large a scale. All the species which Portlock and I unite into the two genera *Phacops* and *Phillipsia* possess a horny membrane, divided into large, circular, hexagonal facets, which generally projects (*Phacops*) in the form of a spherical segment, in the centre of each facet; a crystalline lens is situated behind each facet to which it is united, which, together with the horny membrane, may be separated from the rock. It is probable that a peculiar parabolic transparent substance (*glaskörper*) was situated behind the crystalline lens of each eye, since we sometimes meet with hexagonal loops that penetrate into the rock, after having broken away the crystalline lenses. (Quenstedt in Wiegmann's *Archiv*, 1838.) This structure of the eye we find preserved in the

most various rocks, even in such as are very unfavourable to the preservation of animal remains, and frequently in surprising beauty. Other Trilobites, indeed numerous species, as *Asaphus expansus* and *Illænus crassicauda*, Dalm., and their allies, possess a very different structure of the compound eye from the one just described. The horny membrane in them is perfectly smooth and lustrous, the external upper surface being not at all facetted; instead of this we observe, in well-preserved limestone fossils, specimens possessing a shining and transparent horny membrane, and beneath the latter an extremely fine net, formed of hexagonal meshes. A transversal section of the thin crust exhibits striæ directed perpendicularly to the smooth horny membrane, which are formed by the lateral boundaries of the extremely numerous crystalline cones of the respective eyes. I am not prepared to decide whether the fine reticular delineation has only been produced by the facetted nature of the internal surface of the horny membrane, or, as in *Branchipus*, by a reticulated membrane. As a matter of course, so tender a structure, which can only be observed by the microscope, can be distinctly visible but under particularly favourable circumstances; indeed it has only been detected in well-preserved specimens of the above-named Trilobites and their allies, but by no means in all Trilobites with a horny membrane. [See Quenstedt's above-mentioned treatise 'On the Structure of the Eyes of Trilobites.'] Finally, we have still to adduce a third difference in some species of *Calymene*, viz. in *C. Blumenbachii* and *Tristani*; and also in *Homalonotus*. The first were with general consent united into one genus with the large net-eyed species, although no one has as yet succeeded, as far as I am aware, in observing the structure of the eyes in them. Instead of eyes there is at the locality where we should expect to find them a cavity. I have termed these eyes, in the absence of a more suitable expression, and after the example of Dalman, *Oculi hiantes*. The eye being certainly never concave during the lifetime of the animal, the hole has most probably only been produced after death by the destruction of the eye itself, since it occupies the exact locality where the eyes are wanting in all the other Trilobites. It is most probable that the cause of this easy destructibility of the eyes may arise from the nature of the substance of the horny membrane; a decay of the horny membrane must naturally produce an annihilation of the whole of the eye. Now on comparing the eyes just described with the

corresponding organs of the above-mentioned four genera that were considered as blind, we find that two of them, viz. *Ogygia* and *Conocephalus*, are allied to *Asaphus expansus* and *A. crassicauda*, the two others, *Paradoxides* and *Ellipsocephalus*, are, on the other hand, allied to the last-described Trilobites, viz. to *C. Blumenbachii*. In the former we observe small protuberances at the locality where the eyes are situated in other Trilobites, viz. at the facial suture, which possess the form of eyes, and are covered like them by that part, resembling an eyelid, which adjoins the facial suture. These protuberances want only one thing, namely, the above-described structure of compound eyes. Owing to this last reason the Trilobites belonging to this group have been pretty generally considered as blind. Zenker indeed even went so far on this account as to designate their eyes by a particular term, he called them *winged protuberances*. If all the other Trilobites possessed eyes furnished with large facets, such as we find in *Calymene macrophthalma*, *Asaphus caudatus*, *A. mucronatus* (among the species of the genus *Phacops*), some plausible reasons might be adduced in favour of the assumption which denies the function of eyes to these protuberances. It so happens, that all *Ogygiæ* and *Conocephali* have hitherto been found only in the clay-slate and grauwacke: now a structure of eyes like those of *Phacops* and *Phillipsia* may certainly be preserved in such rocks, as indeed is proved by *Phacops macrophthalmus* (*Calym.*) occurring in the roofing-slate of Wissenbach, by *Ph. proavius* from the grauwacke of Ginec in Bohemia, and by the *Phillipsia æqualis* from the clay-slate of Herborn; but how is it possible to expect a preservation of the microscopically fine structure of the eyes of *Asaphus expansus*, which can only be observed, provided the horny membrane is perfectly transparent, in such rocks as grauwacke and the clay-slate? How could this be possible in rocks of this nature? Supposing even that we had at our disposal not merely impressions in the rock, but the crust or shell of the animal itself, the most we could expect to find would be a tolerably smooth, but not a transparent horny membrane, and yet this condition is absolutely requisite to enable us to observe the compound structure of eyes with a smooth, not facetted horny membrane. It is by no means uncommon to find not the least perceptible structure of the eyes in allies of the *A. expansus* from limestone rocks, which are highly favourable to the preservation of the hard parts of the animal;

which may probably have induced Steininger to ascribe simple eyes to the *Calymene concinna* from the Eifel, but no one has yet entirely denied their former power of vision: such a badly advised scepticism has only been asserted with respect to the Trilobites of the clay-slate and grauwacke. What I have said of *Calymene Blumenbachii* holds good with respect to the other Trilobites which were considered as blind, belonging to the genera *Paradoxides*, Brongn., and *Ellipsocephalus*; they both have a hole which penetrates the upper covering of the cephalic shield at the locality where the eyes were situated, the latter themselves have disappeared. Now whether it is more probable that the eyes have in this case decayed, or been annihilated, and thus left the hole owing to the easy destructibility of the horny membrane, or that the hole was originally there, is a question which, in my opinion, is placed beyond doubt by comparative anatomy.

Now if most of the Trilobites which were formerly considered blind have been proved to have been furnished with eyes like the rest, there still remains a small number in which we have hitherto not been able to trace the existence of eyes. These are the Trilobites designated *Ampyx* by Dalman, and arranged by him under the genus *Asaphus*, and the Trilobites of the genus *Cryptolithus*, Green, *Trinucleus*, Murchison. In neither of them have we yet been able to detect anything like eyes. I have had but poor materials, I regret to say, for my own researches on *Ampyx*; the only specimen in the Berlin Museum exhibited no traces of eyes nor of the facial suture, the casts in plaster of Paris equally as little, and the decriptions of Dalman, Sars and Portlock likewise do not make any mention of either one or the other. This absence of the facial suture leaves us in complete uncertainty as to whether we have really to deal with perfect cephalic shields, or whether the maxillary shield may not have separated itself from the forehead portion in a similar manner, as this is generally found to be the case with *Paradoxides gibbosus* from the slate of Andrarum; the eyelid-like appendage is also wanting in the latter, so that the lateral margin of the forehead portion appears to be rectilinear, and therefore like a perfect cephalic shield. It is very desirable that geologists and palæontologists, who have occasion to collect species of *Ampyx* in their places of deposit, should endeavour to ascertain whether maxillary parts, which have got separated, and belong to the apparently perfect

heads, do not occur. The same may perhaps hold good with respect to *Arges*, Goldf., since the *Odontopleuræ*, which are nearly allied to it, also want the so-called upper eyelid, causing the forehead which has been deprived of its maxillary shield to appear like a perfect cephalic shield (*O. centrina*).

We have still to consider the genus *Cryptolithus*; that its cephalic shield is perfect is beyond all doubt, even if the facial suture had not yet been discovered in it; this suture however really has been detected in its normal course in a stone cast of *Cr. Caractaci* in the Berlin Museum, but there is no trace of eyes, although the facial suture circumscribes as usual the so-called upper eyelid. However, even with regard to this genus, I am induced to hope for a future discovery of the eyes from a Trilobite found in the Goniatite-limestone of Dillenburg, which will be subsequently described; I have named it *Phacops cryptophthalmus* (perhaps the *Calymene lævis*, Münster). It certainly is not impossible that there may have existed blind Trilobites, as we even find living Crustacea deprived of eyes; but it is precisely a more accurate investigation of these latter which proves that all principles of analogy are against the assumption of blind Trilobites. We find, for instance, in all recent crustaceous animals compound eyes; only some genera wholly parasitical, belonging to the order of the Isopoda (*Bopyrus*) and to a division of Entomostraca (*Lernæa, Cecrops*, &c.), are blind. All these blind species are therefore parasites, and indeed such as never quit the place they have once fixed themselves in between the gills of Crustacea or fishes; they are always more or less degenerated in their form, sometimes so much so as to render the recognition of the type of their order a matter of impossibility. The study of their development has however likewise proved with respect even to these animals, at least with regard to those which differ most from the usual type (as for instance *Lernæa*, &c.), that they possess an eye as long as, after their liberation from the egg, they swim about freely; that they however lose this eye in the metamorphosis which takes place when they have attached themselves as parasites. This may probably be the case likewise with respect to *Bopyrus*, a constant parasite and therefore blind wood-louse, which has indeed (if such a thing can be conceived) the most similarity with the Trilobites among the permanently fixed Crustacea. It is also very much deformed. On comparing now our supposed blind Trilobites with those degenerated animals,

which indeed for the greater part are reduced almost to the mere and most necessary organs of existence, those of nutrition and of reproduction, the conviction must at once urge itself upon our mind, that there can be no affinity between them and these parasites. We observe no degeneration in them in any other respect; excepting the eye, they have as perfect a normal development in all other respects as the species furnished with the largest facetted eyes. Many indeed possessed the capacity of doubling themselves up, a power which is as much opposed to the principles of a parasitical life as anything that can be conceived. The existence of spine-like appendages in many of the species of *Ampyx* at the angles of the cephalic shield, and even at the forehead, can likewise not be reconciled with such an assumption. *Cryptolithus*, although not contractile, seems from its form to have been equally as little intended by nature for such a mode of life. Everything indeed suggests to us the necessity of seeking still further for eyes even in these species, and no slight hope of success is held out to us by the fact of *Phacops cryptophthalmus* possessing eyes, although such small ones and situated so nearly on a level with the cheeks, that they can only be detected in the fossil by a practised eye. The fact of blindness is therefore at all events limited to the last-named genera, *Cryptolithus*, *Ampyx* and *Arges*, and even with regard to them forms but a very doubtful characteristic; all the other genera possessed eyes during their lifetime. Some, for instance *Phacops* and *Phillipsia*, possessed a horny membrane furnished with large facets that were even visible to the naked eye; in others, and that in the majority of Trilobites, the eyes were smooth, not facetted externally: and there finally remains a certain number respecting the eyes of which we know nothing, since they were destroyed. To these latter with "*oculi hiantes*" belong the greater portion of the Trilobites which were formerly considered as blind, together with the true *Calymenæ* and *Homalonoti*.

The cephalic shield presents various other important characteristics besides the difference of the eyes, but which have not been taken notice of in drawing up the generic characters. Of these I consider the *facial suture* as the most important. I have already alluded to the cephalic shield as being composed of several pieces connected by sutures. This is a peculiarity of this family, not possessed, to my knowledge, by any other of the crustaceous animals; it will therefore scarcely be surprising to

find generic peculiarities prominently exposed in these sutures. Wahlenberg certainly has already fully appreciated the importance of one of these sutures, the so-called facial suture; and Dalman and Boeck have subsequently followed in his steps; but it has by no means been appreciated by all palæontologists as it deserves. For this reason it will not appear superfluous to enter somewhat more particularly upon the consideration of these peculiar sutures. In the Dudley Trilobite, *Calymene Blumenbachii* (Buckland's 'Geology,' 46, 2), we observe, even on a mere superficial inspection, two generally indented lines, which proceed from the angle in a curved course diagonally over the lateral portions of the cephalic shield, and meet at the anterior margin in an arch coming from both sides; the cephalic shield is frequently divided by them into three different pieces.

This composition of the upper covering of the cephalic shield of three pieces, which are connected in the above-mentioned lines, but which are nevertheless capable of being separated from one another, has been met with in almost all Trilobites; the only genera in which it is not known to occur are *Ampyx* and *Arges*. Corresponding with these parts, the *forehead part* and the two *maxillary pieces*, we find on the under surface likewise three (rarely two?) pieces united by sutures in the same manner, leaving open the central part which is situated beneath the forehead part, as we observe in the axis of the thorax and caudal shield; here the masticatory apparatus was situated, of which however not a trace is met with, with the sole exception of the labrum, resembling that of *Apus cancriformis*. Of the pieces of the lower side, the lateral ones are situated beneath the cheeks, and only separated from them by a narrow cavity; the third odd piece forms the lower part of the anterior margin and bears the labrum posteriorly, which itself again consists of a horizontal part, two-pointed at the extremity, and of two wing-like ascending appendages, which are affixed on each side in the suture between forehead and cheek *. Of all these pieces and sutures only those of the upper surface are valuable for our purpose, since those of the under surface are too rarely accessible to observation. The suture in which the pieces of the upper and lower covering of the head meet is equally of as little value;

* This apparatus, which was first observed by Stokes, was most carefully investigated by Pander, who however was less successful in the interpretation of the parts. (Pander, Contributions to the Geology of Russia, Petersburg, 1830.)

this marginal suture is pretty nearly uniform in all. The suture between the forehead and maxillary parts, the facial suture (*linea s. sutura facialis*), on the contrary, is of very considerable importance. The position of the eyes being invariably close to the facial suture, and indeed in such a manner that the latter separates the real field of vision of the eye from the forehead portion, it enables us to describe accurately the course of the suture. This may naturally be divided into two parts; the one in front of the eye, and the other behind it: at the eye itself it generally circumscribes a particular lobe of the forehead portion, which covers the upper part of the ocular cone (the *upper eyelid* of Dalman), and which therefore enables us to determine the position of the eyes, even in separated maxillary parts and eyes. This so-called eyelid is absent in only very few Trilobites (*Paradoxides*). The course of the facial suture in front of the eye frequently exhibits remarkable differences even in species which are nearly related to one another (*Asaphus extenuatus*, Dalm., and *As. expansus*, Wahlenb.), and is therefore of little consequence; but it is very characteristic for several genera, that the forehead part becomes so broad, and the cheeks proportionately so narrow, that the apices of the latter do not touch, as usual, in front of the forehead; the facial lines of both sides do not meet in that case, but terminate in the marginal suture. The facial suture and the cheeks might be separately called in this case *genæ s. lineæ faciales discretæ*. This occurs in *Ellipsocephalus Hoffii*, in the most distinct manner; it may also be seen however in *Amphion*, *Illænus*, and in some of the *Asaphi*, also in *Calymene Blumenbachii*. The direction of the suture behind the eye, on the other hand, presents very important differences. In *Illænus* it proceeds in a tolerably straight direction towards the posterior margin; more frequently it runs at first pretty parallel for a shorter or greater distance with the posterior margin of the cephalic shield, and then terminates at the external margin; it joins this latter, sometimes forming a right angle, sometimes under a more or less acute angle, from its changing its direction towards the end, and running backwards for a, generally, short distance. This is the course in *Phacops*. Intermediate between *Phacops* and *Illænus* are the genera *Calymene*, Brong., *emend.*, *Homalonotus* and *Conocephalus*, in which the facial line terminates in the two angles of the cephalic shield. Its most frequent course however is that of a curve, the convexity

of which is directed exteriorly and anteriorly near the posterior margin. We have therefore to distinguish a threefold direction of the facial line, starting from the posterior angle of the eye: —1st, towards the external margin; 2ndly, towards the angle; and, 3rdly, towards the posterior margin of the cephalic shield.

Another characteristic furnished by the cephalic shield likewise deserves attention, namely, the structure of the *frontal part* (*Stirn-theil*). It is only in few species that this part is uniformly arched, as in *Nileus* and *Bumastus*; generally speaking this also is tripartite. The two axal furrows of the body, which define the boundary between axis and fins, are continued over the cephalic shield; in that case it is only in *Illœnus crassicauda* that they end without meeting; however they generally meet and inclose the central part (which is usually arched) the so-called *frontal protuberance* or *glabella*. As each protuberance on the upper surface of the shell of the body, both in the shell of Trilobites as in that of recent Crustacea, corresponds with an indentation on the lower side, and *vice versâ*, the form of the *glabella* may not be without importance; indeed it rather indicates essential differences of internal organization. Were we to find powerful jaws, we should be led to seek the places of application of the muscles moving them in some of these impressions, which are represented on the upper surface by protuberances; but the accessory parts of the mouth, every vestige of which has disappeared, scarcely required a highly developed muscular apparatus, and it is probable therefore that a portion of the more important intestines, the relative development of which caused the different vaulted appearances at various places on the cephalic shield, were situated beneath these elevations. But whatever may have produced the shape of the frontal part, it must be admitted to form an important characteristic. Its differences are of a twofold nature; first, as to its dimensions; secondly, as to its articulation. It is either broadest towards the anterior part, that is clavate, which is most frequently the case; or it becomes narrower anteriorly, and has its greatest width at the neck, which is called conical or truncately conical; in some few it is uniformly broad everywhere; in still fewer instances it is cylindrical and enlarged at the centre. It exhibits a second difference with regard to its more or less simple structure; in some it is perfectly simple (*Homalonotus*), and only intersected in the neck by the posterior marginal or neck furrow; generally speaking it is di-

vided by lateral incisions into *lobes*, of which there are then three on each side*.

Behind the head is situated the articulated thorax, in which the differences are limited to the number and structure of the rings. The number of rings is definite and constant in each species, according to a law deduced by Wahlenberg from numerous observations; Dalman found the same in all the species investigated by him, and Professor Quenstedt has likewise confirmed it more recently. It is therefore no longer a contestable fact, and we should rather ascribe the uncertainties of number, which we still occasionally meet with in books, not to the nature of the animal, but rather principally, if not exclusively, to the imperfect condition of the fossils, and to the consequent difficulty in counting the joints. The posterior margin of the cephalic shield, which is formed by the furrow of the neck, as also the similarly shaped anterior margin of the tail, have frequently given rise to a false calculation of the rings of the thorax. Their number is decidedly fixed with respect to the individual species, but whether it is so also with regard to the genera is another question. In many cases there can be no doubt of it, in favour of which assertion we may adduce the partially natural groups which Quenstedt obtained by placing together the species with equal numbers of joints. Six thoracic rings, the smallest known number, occur in *Ampyx* and *Cryptolithus*; seven only in *Ogygia*; thirteen is a characteristic number for *Calymene* and for *Homalonotus*, so nearly related to it; eleven for *Phacops*. It is different however with respect to the 8-, 9- or 10-jointed Trilobites, which Dalman enumerates in his divisions of *Asaphi genuini ecaudati* and *mutici*, *Nileus* and *Illænus*, to which Murchison's *Bumastus* is most nearly related. Are we now to unite all these Trilobites in one large genus, *Asaphus* (*Cryptonymus*, Eichw.), as I have done, subsequently dividing the latter into subgenera, or should they be divided according to the number of joints, leaving other reasons of division out of consideration? The latter view is the one generally entertained; indeed some persons have gone further, and have

* These sections, the number of which, including the neck furrow, never exceeds four, may lead us to infer the real number of rings, of which we may conceive the cephalic shield to be formed. The posterior margin of the cephalic shield has entirely the shape of a common ring of the thorax; and in some few the two hindermost sections of the frontal protuberance likewise form a second ring.

even ascribed the rank of genera to the sections based upon the more or less deep longitudinal and transversal furrows. It is my conviction that this must lead to an objectionable subdivision. Thus we distinguish now true *Asaphi* (*Cryptonymus*, Eichw., a part of them at least), *Isotelus*, *Symphysurus*, *Nileus*, *Illænus*, and *Bumastus*. If the 9-jointed *Illænus centrotus* possessed one joint more, it would remove all doubts at once; the 8-jointed species of *Asaphus* would in that case unquestionably form with *Isotelus* and *Nileus* a distinct genus in the more narrow sense of the word, and the 10-jointed *Illænus* and *Bumastus* another; to the former we might leave the name of *Asaphus* assigned to it by Brongniart, to the latter the name of *Illænus* might be given, although many 8-jointed species approach nearer to the 10-jointed in habit than to others of the division; for instance, *Illænus*, and *Asaphus palpebrosus*, which M. von Buch on that account likewise considered as belonging to *Illænus* (Contributions to the Geology of Russia, p. 51). In this case we should have to regard the species of the two genera as two parallel series, made up of corresponding forms, as we see similar parallel series of genera exhibited in whole families; for instance, the series of the Nautilaceous genera (*Orthoceratites*, *Cyrtoceratites*, *Nautilus*) are repeated in the family of the *Ammonites* (*Baculites*, *Hamites*, *Ammonites*). The species of *Nileus* would in that case *be analogous* to *Bumastus*, *Asaphus palpebrosus*, &c. to the *Illæni*; *Asaphus extenuatus*, however, would be analogous to *Illænus centrotus*; only *Asaphus expansus* and the *Griffithides* would not exactly correspond. But the often-mentioned *Illænus* has not ten joints, but only nine, according to the statement of the accurate and careful Dalman, both in the diagnosis of the species and section. Nevertheless, we might still be in doubt about it, notwithstanding the accuracy of Dalman, who would certainly have put a mark of interrogation in any doubtful case, if another observer equally credible, Capt. Portlock, had not likewise represented two Irish specimens of the same species with nine thoracic rings. If therefore we were to unite only species possessing an equal number of thoracic rings into one genus, there would be no alternative but to separate this last-named trilobite, for instance, from its next of kin "*Illænus crassicauda*," with which it completely corresponds in point of habit, form of forehead, course of the facial line, position of eyes, structure of the rings of the thorax and of

the caudal shield, and to form a new genus of it, which however would be solely distinguished by the number of the thoracic rings. The difference of the two genera would certainly not be less than that existing between the two genera *Porcellio* and *Oniscus*, of which the one possesses 7-jointed external palpi, the other 8-jointed ones. Such a splitting up of closely allied species appears to me however purely artificial, and therefore unjustifiable. I consider even the uniting of all 8-, 9- and 10-jointed Trilobites into one genus as more natural than such a division, the more so as, with all the difference of the extreme forms, we find them linked together by the intermediate forms of *A. palpebrosus* and *A. læviceps*. All these 8-, 9- and 10-jointed Trilobites are unquestionably more nearly related to one another than the genera *Nuttainia*, Portl., *Brontes*, *Gerastos*, Goldf., and *Phillipsia Dalmani*, to the 10-jointed Trilobites (*Illænus* and *Bumastus*), although they all possess the same number of joints, namely 10. The Trilobites just enumerated prove most evidently, *that Trilobites which are widely different from one another may nevertheless correspond in the number of thoracic rings. Illænus centrotus*, on the other hand, as also the 10-jointed *Asaphus Dalmani*, which correspond in all the other generical characteristics with the 9-jointed *Phillipsiæ* of Portlock, make it appear suitable to unite, by way of exception, Trilobites with an *unequal number of joints* into *one genus*.

The differences in the structure of the rings of the thorax are not very numerous; I will only remark that we are able to draw inferences with perfect certainty from their structure as to the existence of the power of contraction. It is by no means uncommon, that Trilobites which have possessed the power of doubling themselves up into a perfect ball, are found in an extended position, and if this was to be considered as a proof of the want of contractibility, it would frequently lead us into serious errors. It is therefore not unimportant to possess a character which may guide us to a safe decision. Such a character exists. The margins of the fins, for instance, have so fine an edge in all the contractile species, that this sharpened anterior margin of the posterior joint is enabled to insert itself beneath the posterior margin of the preceding joint; the front fin, when in the act of contraction, inserted itself beneath the posterior margin of the cephalic shield; the anterior margin of the caudal shield, on the other hand, under the last joint of the thorax. This

sharpening of the margin by a surface which becomes broader and broader from the interior externally, admits of our forming an opinion as to the existence of the property of contractility, even in straightened individuals. The contractile power certainly depended in a still higher degree on the structure of the joint between the articulations of the axis, but since all Trilobites were able to bend and extend the whole body, the difference in the formation of the joint can only be a relative one, and therefore one that is difficult to handle; this is not the case with the fins. Brongniart, and several later authors, have laid great stress on the absence or presence of the power of contraction, and certainly not without reason. It is most characteristic for several genera; but what I endeavoured to prove with regard to the number of individual joints also holds good in the present instance, viz. this character is likewise not of equal value throughout the whole family. As an instance of this, I will mention *Odontopleura*, a genus which I have recently established, differing from all other Trilobites in habit as well as in several characters. Of the three species with which I have hitherto become acquainted, one, *O. bispinosa*, was entirely deprived of contractile power, whilst a second, *O. crenata*, could double itself up completely; the third however *O. mutica* could only press cephalic and caudal shield against each other, and double itself up imperfectly. These three species therefore exhibit every degree of contractility, and yet they undoubtedly belong (as will be seen from the subsequent descriptions) to one genus, and are not mere analogous forms of different genera. Even in the genus *Phacops* we find species with and without the power of contraction. The genera *Calymene*, Brongn. *emend.*, *Homalonotus*, *Asaphus*, Brongn. *emend.*, *Illænus Dalmani*, on the other hand, only contain contractile species with fins that are sharpened at the anterior margin and rounded at the extremity; *Ogygia* (the 7-jointed Trilobites of Quenstedt), the *Paradoxides*, *Cono-* and *Ellipso-cephalus*, *Nuttainia*, and *Brontes*, contain only species that do not possess the power of contraction, with fins that are not at all, or hardly, sharpened at the anterior margin. The apices of the fins are drawn out into long spines in some few species of different genera (*Phacops arachnoideus* and *Odontopleura bispinosa*), a peculiarity which has been proved to be of secondary importance, since *Odontopleuræ* have been found without spines. In addition to this, the rings of the thorax also exhibit differences in the

depth of the transversal furrows, which are entirely wanting in *Illænus*, but, above all, in the greater or slighter perfection of the joint between the articulations of the axis, and the free fins belonging to them, which joint disappears altogether in *Bumastus* and *Nileus*.

I shall now conclude with a few observations on the *caudal-shield*. I have already stated that it consists of rings, which are only distinguished from those of the thorax by their being coherent with one another. This cohesion differs considerably in degree; the most various intermediate stages exist between the caudal shield of *Nileus*, in which neither axis nor fins, and still less their articulation, is perceptible; and *Amphion*, in which the coherent rings of the tail have so great a resemblance to the posterior rings of the thorax, that they can scarcely be distinguished from them. This similarity renders the counting of the individual thoracic rings exceedingly difficult in some cases, and the erroneous statements in this respect may frequently be traced to this circumstance. The number of joints of the tail is certainly equally constant for every species, as it is with respect to those of the thorax; their determination, however, is far more difficult than in the latter. The observations hitherto made do not yet sufficiently indicate what proportion the numbers of the rings of the tail and thorax bear to one another in the different species; I certainly ascertained from some former researches which I instituted on this point, that the number of rings of the tail and thorax, in some species at least, is equal to that of all the rings of *Paradoxides Tessini*; and this may be the case with a great part of the family. Some, on the other hand, have evidently a smaller, and others even a larger total number, and I must for the present leave it undecided, whether in the former case the joints are coherent, or whether in the latter they are a multiple of the number of joints of the already mentioned *P. Tessini*. This is a question which certainly deserves more accurate investigation.

The preceding observations are not intended to form a complete natural history of the Trilobites; a profound work on this subject may soon be expected from one of the most distinguished investigators of recent Articulata, Professor Burmeister. My remarks are only intended to justify those alterations which I have proposed in the systematic arrangement, and, if possible, to confirm them.

II. *On the Genera of the Trilobites.*

In point of their systematic position, I regard the Trilobites as constituting a peculiar order of Crustacea, at present perfectly extinct, and which certainly connects the two divisions of the *Malacostraca* and *Entomostraca*, but approximating nearer to the latter than to the former. They are related to the former by their calcareous crust-like shell, and by their not possessing simple eyes in conjunction with compound eyes. The wood-lice have the greatest similarity to them among the divisions of the shelled Crustacea. *Limulus* and *Phyllopoda* are the two orders among the *Entomostraca*, to which they are united by the nearest characters of affinity. They correspond with these two orders in point of form and size of the clypeoid head; and, moreover, with the latter as regards the rings of the thorax, which are moveable, and vary in point of number. The soft texture of the under side of their body, and the circumstance that no one has as yet succeeded in detecting unquestionable vestiges of legs, are in favour of the supposition that they must have corresponded likewise in the structure of their feet with *Apus* and *Branchipus*. Nor have we as yet any positive knowledge with regard to palpi. Portlock has certainly discovered an articulated member close to the forehead of *Nuttainia hibernica*, which he compares to an antenna; but this discovery is of too isolated a nature, and requires further confirmation. The constant sutures of the cephalic shield, the so-termed facial sutures, are wholly peculiar to the Trilobites.

In the following synopsis I have classified all the genera of Trilobites into five groups or families, which may be again subdivided into two sections.

Section I. With a *caudal shield* situated behind the articulated thorax, and formed of perfect rings, but which are more or less coherent.

Family I. *Trilobites with granular facetted eyes.*—The eye has a facetted horny membrane, the facets being visible even to the naked eye. Glabella distinct, frequently strongly arched, generally broader anteriorly, *clavate*, more rarely cylindrical, sometimes rather narrower anteriorly, lobed at each side by four furrows, the anterior odd lobe (*frons*) is largest. This frontal part is very large in some, of a more or less *trapezoidal* shape, and

extends almost as far as the furrow of the neck; the lateral lobes in this case disappear almost entirely. Thorax 9-, 10- or 11-jointed, joints furrowed, caudal shield with an articulated axis and ribbed sides.

This family is identical with Quenstedt's group of 11-jointed Trilobites, in his treatise above alluded to. Although the law he has laid down in it, namely, that all Trilobites with a facetted horny membrane are 11-jointed, has not been confirmed, as, in addition to the 10-jointed *Asaphus Dalmani*, which was known at that time, other 9-jointed species have subsequently been discovered, having the same structure of eyes, yet it cannot be denied that this mode of classification is the first important step towards an improvement of Brongniart's system. According to the course of the facial suture, the hitherto known species of this family are divided into two groups.

I. *Phacops*, m. (φακὸς, *the lens*, and ὤψ, *the sight, eye*). *Facial suture extends to the external margin. Thorax* 11-*jointed.*

Professor Goldfuss has subdivided this genus established by me into three genera (*Phacops*, *Asaphus*, *Acaste*), but more according to habit than zoological characters. I certainly do not agree with this tripartite division, but nevertheless consider a further division of this genus as practicable. Brongniart arranged a part of the species united here in the genus *Calymene*, another part he placed among the *Asaphi*; all the allied species that were subsequently discovered were distributed according to the *habit* in a similar manner among the two genera. The differences in appearance of species, which caused for so long a time the separation of nearly related Trilobites from one another, and their union with others widely distinct, must necessarily be associated with geological differences. I believe I have discovered two essential distinctions between *Calymenæ* and *Asaphi* of our genus, which however require further confirmation; the one consists, in my opinion, in the presence or want of contractility, the other in the number of rings which form the caudal shield; in the latter, the *Asaphi*, they appear to amount to double the number possessed by the former. The difficulty, sometimes indeed the impossibility, of counting the hindermost rings of the tail, forms no trifling obstacle against the discovery of the numerical law here alluded to. The greatest number of rings of the tail known to me is in that of *Asaphus Hausmanni*,

in one specimen I counted twenty-two; in all the species nearest related to it, with which I am acquainted, the number is certainly smaller, but always exceeds eleven. In *Ph. macrophthalmus* and in other species considered as belonging to the *Calymene*, on the other hand, I always found their number below eleven, but I never met with the joints of the axis distinctly visible to the most extreme point of the axis, as is the case in *A. Hausmani*. Taking these distinguishing characters as a basis, I for the present divide *Phacops* into two subgenera, leaving it to be decided whether they do not merit the rank of independent genera for further researches.

A. *Phacops* in the restricted sense (*Calymene*, Brong. in part). *Contractile.* Fins rounded at the extremity, with an acutely sharpened anterior margin. Caudal axis furnished with 11 or fewer joints.

Ph. macrophthalmus, Brong., *protuberans*, Dalm., *cryptophthalmus*, m. (*Calymene lævis*, Münst. ?), *sclerops*, Dalm. (*Powisii*, Murch.), *conophthalmus*, Boeck, *Downingiæ*, Murch. (Pl. IV. fig. 2.), *proavius*, m (Pl. IV. fig. 3.), *rotundifrons*, m.

B. *Dalmania* (*Asaphus*, Brong. in part, *Asaphus*, Goldf.). Not contractile: fins at the anterior margin scarcely sharpened, frequently acute. Forehead always clavate, distinctly lobed. Caudal shield furnished with more than 11, sometimes with as many as 22 joints of the axis, frequently elongated at the extremity of the tail.

Ph. caudatus, Brünn, *mucronatus*, Brong., *Hausmanni*, Brong. (Pl. IV. fig. 1.), *odontocephalus*, Green (Pl. IV. fig. 4.), *truncato-caudatus*, Portl.

II. *Phillipsia*, Portl. *Facial suture extending to the posterior margin. Forehead almost cylindrical. Thorax* 9- *to* 10-*jointed.*—Carboniferous formation.

a. Nine-jointed species: *Phacops Kellii, Jonesii, ornata* (Pl. IV. fig. 7.), and other species discovered by Portlock in the Irish mountain limestone. The facial suture is not yet known in all the species considered as belonging to this group.

b. Ten-jointed species: *Asaphus Dalmani*, Goldf., from the Carboniferous limestone of Ratingen. Differs from *Phacops* (with which Professor Goldfuss has recently united it) in the number of thoracic rings and facial suture.

I am not aware of a more suitable place in the system for *Calymene æqualis* von M. (Pl. IV. fig. 6.) (from the slates of Herborn, the number of joints of the body of which are as yet unknown) than the present, but it bears about the same relation to the preceding as to the number of the rings of the axis of the tail, as *Phacops macrophthalmus* to *Dalmania*.

Family II. *Asaphi*.—Eyes with a smooth horny membrane. Facial suture terminating at the posterior margin. Body from 7 to 10-jointed.

This family contains Brongniart's genera *Ogygia* and *Asaphus*, after excluding the species considered as belonging to *Phacops*. It is distributed like the preceding through all the divisions of the transition rocks, with the exception of the *Paradoxides* slate and the lower sandstone of the North, but it is more abundant in species and genera in the lower strata.

A. *Asaphi* in the restricted sense. Contractile species. Fins always sharpened at the anterior margin, generally obtuse at the extremity.

III. *Griffithides*, Portl. Glabella tumescent, clavate. Thorax 9-jointed. Caudal shield furnished with 10 joints and upwards.—Coal measures. Mountain limestone.

Gr. globiceps, Phill. (Pl. IV. fig. 11.), *longispinus*, Portl., *obsoletus*, Phill.—Coal formation of Altwasser, &c. of Upper Silesia.

IV. *Gerastos*, Goldf. (*Proteus*, Stein.) Glabella truncate, cylindrical, indistinctly lobed. Thorax 10-jointed. Tail less and indistinctly jointed.

G. concinnus, Dalm., &c. In the younger Silurian and in the Devonian strata, and perhaps also in the Carboniferous limestone (Visé).

V. *Asaphus*, Brong. Glabella well-defined, clavate until it disappears; the articulation of the tail is likewise distinct or indistinct until it disappears completely. Body 8-jointed.

The species belonging to this genus have been divided into several genera, which are certainly readily distinguishable in their extreme forms, but are connected with one another by intermediate members. Professor Goldfuss divides them into the four genera, *Cryptonymus*, *Isotelus*, *Nileus* and *Symphysurus*, which however only differ in certain degrees. *Asaphus* is a characteristic genus for the older Silurian formations, together with the following.

VI. *Illænus,* Dalm. *emend.* Without glabella and without articulation of the tail. Body (9) 10-jointed. Joints smooth. Eyes distant from the axis of the head, situated nearer to the margin.—Silurian.

Besides the already known species, viz. *I. crassicauda* and *centrotus,* I consider *Bumastus Barriensis,* Murch., as belonging here.

B. *Ogygiæ.* Not contractile. Caudal shield large, articulated, generally very much flattened. Glabella clavate.

VII. *Ogygia,* Brong. *emend.* Body 7 (?) 8-jointed.

O. Guettardi, Brong., *Desmarestii,* Brong., *Buchii,* Brong., *dilatata,* Brünn (Pl. IV. fig. 9.). Characteristic for the lower Silurian strata.

Asaphus tyrannus, Murch., does not belong here (to which division I have referred it in my 'Dissertation'), but to *Asaphus.*

VIII. *Brontes,* Goldf. Caudal shield clypeoid, with radiating ribs. Body 10-jointed.

Br. flabellifer, Goldf., &c. Characteristic for the Devonian rocks.

IX. *Nuttainia,* Eaton, Portl. Fins of the caudal shield distinct, connected only by their margins, terminating in triangular points. Body 10-jointed.

N. hibernica, Portl. (Pl. IV. fig. 8.).—Ireland. A perfectly corresponding species occurs at Lockport in North America.

Family III. *Calymenæ.*—Generally with "oculi hiantes," smooth horny membrane seldom preserved, reniform, not seated on conical protuberances. Facial suture extending to the covering of the cephalic shield. Glabella distinct, generally narrower towards the anterior portion. Body 12-jointed and upwards. Joints furrowed. Caudal shield articulated. *Ellipsocephalus* alone forms an exception.

A. *Genuine Calymenæ.* Possessing the power of contraction.

X. *Encrinurus,* nov. gen. *οὐρὰ, the tail,* and *Encrinites.* Eyes smooth. Glabella clavate. Caudal shield furnished with a many-jointed axis and few fins.

Entomostracites punctatus, Wahlenb., differs so much from all other Trilobites, that it well deserves to form a particular genus; it unites the clavate forehead of the *Asaphi* with the course of the facial suture and shape of the eyes of *Calymenæ.* It forms

a transition from the latter genus to *Phacops* by means of the facial suture. I have given it the above name on account of its peculiar caudal shield. Two species of Portlock, viz. *Amphion multisegmentatus* and *Ogygia rugosa*, in this respect likewise belong to it.

XI. *Amphion*, Pand. Eyes smooth. Glabella of equal width, lobed. Body many-jointed (20-jointed); caudal shield small and distinctly articulated.

A. frontilobus, Pand. Portlock combines, together with *Amphion*, some species not belonging to this genus; *A. gelatinosus* belongs to *Phacops*. I have already mentioned others.

XII. *Calymene*, Brong. *emend.* With *oculi hiantes*. Forehead narrowest anteriorly, lobed. Body 13-jointed. Caudal shield articulated. Ribs mostly furcated.

C. Blumenbachii, Brong. (Pl. IV. fig. 10.), *Tristani*, Brong. (distinguished from the former by the margin of the forehead, which projects in the form of a snout and is curved upwards.)

XIII. *Homalonotus*, König (*Trimerus*, Green). The same as XII., but the glabella is not lobed.

H. Knightii, König, *Herschelii*, Murch., *delphinocephalus*, Green.

B. *Paradoxides*. Not contractile.

XIV. *Conocephalus*, Zenk. Thorax 14-jointed; eyes smooth (?), in other respects like XI.

Sulzeri, Schloth., *striatus*, m.—Bohemian grauwacke.

XV. *Ellipsocephalus*, Zenk. Forehead broad, glabella narrow, almost of equal breadth, rounded at the anterior part, not divided into lobes. Cheeks very narrow, widely distant. Body 12-jointed. Caudal shield small, with a distinct axis, but without articulation.

E. Hoffii, Schl.—Bohemian grauwacke.

XVI. *Anthes*, Goldf. Glabella lengthened semi-elliptically, divided into lobes. Maxillary shields? Eyes? Thorax 12-jointed, with short, acute fins. Caudal shield with a 3-jointed axis and an even border tridentate on each side.

A. scarabæoides, Wahlenb.—Andrarum.

XVII. *Paradoxides*, Brong. *emend.* (*Olenus*, Goldf.*). Gla-

* Zenker was the first (in 1828) who proposed a classification of the *Paradoxides*, the name *Olenus* should therefore be retained for the *Parad. Tessini*, as Zenker named it.

bella somewhat narrow anteriorly. Eyes concave. Maxillary shields generally detached, horned. Thorax 15(?)-jointed. Fins longer than the breadth of the axis, acute. Caudal shield with an articulated axis and ribbed sides, frequently dentated at the margin. Aluminiferous clay of the North.

P. gibbosus, Dalm., *latus*, Boeck, &c.

Family IV. *Odontopleuræ*.—Facial suture terminating at the posterior margin more or less distant from the angles of the cephalic shield. Eyes smooth. Glabella narrow anteriorly, divided into lobes at the sides. Margin of the cephalic shield dentated. Thorax 8-, 9-jointed and upwards. Caudal shield considerably smaller than the cephalic shield, with longer or shorter spiny appendages. The fins of the thorax are likewise frequently elongated into spines.

Although the forms which we have here arranged together correspond very much in habit, and possess distinguishing characters from others, the appearance of a perfectly analogous form among the species of *Phacops* (*Ph. arachnoideus*, Goldf.) is nevertheless very remarkable.

XVIII. *Odontopleura*, m. (*ὀδοὺς*, *the tooth*; *πλευρὰ*, *the rib*). Glabella semicircular. Facial suture, see above. Eyes smooth. Body 9-jointed. Caudal shield furnished with a 2-jointed axis and dentated or spiny margin.

1. *O. bispinosa*, m. (Pl. IV. fig. 12.) (*ovata*, m. Dissert. inaug.) Fins elongated into two long spines.—Northern drift: Upper Silesia. 2. *O. mutica*, m. Semi-contractile. Fins scarcely pointed at their extremity. Cephalic and caudal shield coarsely serrated.—From the same locality. 3. *O. crenata*, m. Contractile. Margin of the cephalic shield curved.—Gothland. 4. *O. centrina* (*Cal.*), Dalm. 5. *O. dentata*, Goldf.

XIX. *Arges*. Eyes? Facial suture straight posteriorly. Cheeks? Body 8-jointed. Caudal shield with an indistinct 4-jointed axis. All the fins are serrated.

Family V. *Trinuclei*.—Head with a broad even reticulate foveolate margin, which is lengthened into horns posteriorly. Surface of the thorax horizontal, only curved downwards with the apex. Facial suture terminating at the posterior margin. Eyes generally unknown.

XX. *Cryptolithus*, Green (*Trinucleus*, Murch.). Glabella clavate, divided into lobes at the sides. Thorax with six segments. Caudal shield articulated. Eyes? Characteristic for the older Silurian rocks, less frequent in the younger.

Cr. granulatus, Green, *Caractaci*, Murch., &c.

XXI. *Ampyx*, Dalm. Only distinguished from XX. by the absence of the reticulate foveolate broad margin. Facial suture? Contractile.

A. nasutus, rostratus, Sars, *mammillatus*, Sars.

Harpes, Goldf. differs from *Trinucleus* by the greater number of rings of the thorax, which latter however cannot be distinguished from those of the articulated tail.—Devonian.

Section II. All the segments of the body at the posterior part of the cephalic shield are homologous and moveable: only the last (rectum) joint is without fins. They are the Myriapoda among the Trilobites, but are not so isolated as the former; on the contrary, we may say that they approximate to the *Calymenæ* through *Amphion*, to the *Trinuclei* through *Harpes*, and finally, to the *Odontopleuræ* through *Odontopleura centrina*. Only one family.

Family VI. *Oleni*.

XXII. *Olenus*. Cephalic shield cornuted. Facial suture terminating at the posterior margin. Glabella clavate, divided into lobes. Eyes hiant, with an upper eyelid. Body (at least when aged) 20-jointed, with a scaly-formed rectum joint. The *Oleni* probably underwent a metamorphosis in as far as the number of thoracic rings increased with age.—In the oldest Silurian rocks.

Ol. Tessini, C.

XXIII. *Remopleurides*, Portl., differs from XXII. only by a lesser number of rings (12), and by the fins being very short in proportion to the axis; in all other respects they correspond entirely with those of the preceding genus.—Irish Silurian transition rock.

R. Colbii (Pl. IV. fig. 13.), *longicaudatus, lateri-spinifer*.

Supplement XXIV. *Ceraurus*, Green.

XXV. *Agnostus*, Brong. (*Battus*, Dalm.), *pisiformis*, Brong.—Lowest Silurian rock.

III. *On the Distribution of the Trilobites in the Strata.*

The Trilobites belong to the oldest class of animals that we are acquainted with; they are restricted to the first of the three principal groups into which we may arrange the long series of fossiliferous formations, namely to the palæozoic rocks. Assertions of the discovery of this class of animals, both in the recent state and likewise in the younger strata, have been made, but every one of these statements has proved to be unauthenticated and erroneous. The newest deposits in which they have hitherto been found to occur is the lower coal formation, the fundamental rock of the coal beds, the mountain limestone of the British Islands, and the equivalent strata of the continent. No trace of them has as yet been discovered in the Zechstein formations: for that which Von Schlotheim described as *Tril. bituminosus* are the gum-teeth of a fish (*Janassa*), as was subsequently recognised by Count Münster, who gave a more accurate representation of them. Lower downwards, however, they have been found through almost all the subdivisions of the transition rocks. Within these limits, which, comparatively speaking, are restricted, they are found widely distributed throughout the known earth, abounding in species and genera, at many localities in almost inconceivable numbers. They belong therefore to the most important inhabitants of those oceans in which the subdivisions of the palæozoic rocks were deposited. The structure of their eyes, which entirely corresponds with the structure of that organ in recent marine Articulata, affords us a proof that the water of those oceans and the supernatant atmosphere must have been equally as transparent a medium at that time as it is at the present day, and that therefore no material permanent alteration can have resulted in either during the thousands of years which have elapsed since the creation of the animal world on this earth.

It is perhaps well to commence with the Trilobites in the palæozoic rocks in the countries surrounding the Baltic.

1. *Countries adjacent to the Baltic.*—The succession of strata of the different subdivisions of the transition rocks is nowhere so evident and striking in any part of the globe as in the countries on the Baltic. It need not be matter of surprise therefore that Linnæus (in his 'Journey through West Gothland,' 1765, p. 21, &c.) makes us acquainted with the entire

order of succession of the strata constituting the Swedish transition formation; and that (long before Murchison's researches diffused a new and clearer light upon the whole system of the palæozoic rocks) Wahlenberg (*Acta Upsal.* tom. viii.), and subsequently Dalman, described with great accuracy the distribution of the Trilobites in the rocks of Sweden. The palæozoic strata have in South and Central Sweden an uninterrupted horizontal position (such as they are everywhere met with in the North of Europe), but exposed at numerous localities by inundations, the younger strata having been washed to a considerable distance. The succession of strata may be best observed at those localities where a protective covering of basalt opposed a greater resistance to those destructive powers. All the isolated mountains, rearing their heads like castles from the level and hilly country of East and West Gothland, bear a basaltic crown on their summit, and the separate subdivisions of the transition formation appear like the steps of a gigantic ladder. This scalariform appearance of the horizontally deposited strata seems to be nowhere more striking than at the Kinnekülle, a celebrated mountain on the east shore of the Wener Lake. The transition rock there consists of the following subdivisions in an ascending order:—at the lowest portion, which at other places rests on gneiss, we find,—1st, a siliceous sandstone, from which however no fossils are known. Thereupon follows, 2ndly, a slaty limestone, which is highly bituminous, and passes into brand and alum-slate with beds of stinkstein; 3rdly, a stratum of considerable depth, principally gray limestone, sometimes pure (marble), sometimes rather marly; this is the richest bed of the Swedish *Trilobites*, *Orthoceratites* and other fossils. Uppermost and covered by trap, there finally occurs a second slaty formation, clay and marl slate of the Möseberg. This is the succession of the strata which Linnæus observed on the Kinnekülle, at the Möseberg, Billingen and other localities. The subsequent researches of Wahlenberg, Hisinger, &c., have added no new member to it on the continent; the entire Swedish continent exhibits the same development from Dalecarlia to Schönen. It is only in the south, known above all by the numerous fossils of its alum-slate at Andrarum, that the rocks exhibit a deviation, the principal limestone acquiring a black colour from the intermixture of coal.

We find the same system of division of the palæozoic rocks on

the east as on the western side of the Baltic, on the coasts of Livonia, Ingermannland and in Karelia. Eichwald (*Iter per Ingriam*, Casani, 1828), Pander (Contributions to the Geology of Russia. Petersburg, 1830), and, in the most recent period, Blasius (Journey through Russia, 1843, vol. i.), have described the same succession of strata in the neighbourhood of Reval and Petersburg; it only deviates from it in so far that the upper clay-slate is wanting, and a blue clay forms the basis of the lower sandstone instead of the crystalline slate rock, a peculiarity which would have been considered incredible some years ago. The sandstone is not so poor in fossils as it is in Sweden, but some strata are found to consist almost solely of very remarkable minute Brachiopoda (the *Ungulites* of Pander), even the cementing medium being wanting. I am not acquainted with any fossils from the alum-slate which rests upon the sandstone.

There are some islands in the Baltic situated between the Russian and Swedish shores, viz. Ösel near the Russian, and Öland and Gothland near the Swedish shore. The two former, Ösel and Öland, are formed of the Trilobite and Orthoceratite limestone; on Öland, the other subdivisions have likewise been found at the base. On Gothland, on the other hand, we meet with a fifth formation, a limestone abounding in fossils, which Hisinger already looked upon as a younger link of the transition rocks. It has not yet been positively ascertained whether a representative of it is also to be found in Russia. The limestone alluded to of Gothland rests upon a sandstone which contains two Brachiopoda (*Orthis pecten, Terebr. reticularis*), which are frequent in the clay-slate of West Gothland. These five subdivisions of the northern transition limestone may all be characterized by Trilobites. The alum-slate by the genera *Paradoxides*, *Olenus* and *Battus* (*pisiformis*); this slate, on the other hand, is entirely deficient in fossils in Russia. The principal limestone contains the genera *Asaphus*, Brong. *emend.*, *Illænus*, Dalm. *emend.*, and *Amphion*, Pand. The following genera are found with equal frequency on both sides of the Baltic: —*A. expansus*, *Illænus crassicauda*, more rarely *A. armadillo*: a facetted Trilobite, viz. *Phacops sclerops*, Dalm., is likewise met with throughout the whole northern European transition formation. There are only two species which, according to Dalman, are common to both the upper strata of this limestone and to the slates of the Möseberg, viz. *Phacops mucronatus* and *Trinucleus*

granulatus, Wahlb. These last-mentioned slates, which have not yet been met with in Russia, are characterized by the common *Ph. mucronatus*, with which some other peculiar forms are likewise associated, viz. *Nuttainia laciniata* (Lich.), Dalm., and *Odontopleura centrina* (*Cal.*), Dalm. The limestone of Gothland contains a greater number of characteristic forms, viz. *Calymene Blumenbachii*, *Encrinurus punctatus*, *Gerastos concinnus*, *Phacops caudatus*, and *Odontopleura crenata*, n. sp. There are therefore but few northern Trilobites found simultaneously in several members of the palæozoic series; on the contrary, they are rather restricted to individual subdivisions, in which, however, they occur in the greatest horizontal extension. The Russian and Swedish transition rocks exhibit the most beautiful coincidence in respect to the Trilobites, as well as in their other fossils (*Orthoceratites*, *Brachiopoda*, *Crinoidea*). This coincidence no doubt extends likewise to the transition rocks of Southern Norway, which abounds in fossils; at least the same fossils have been found in them as in Sweden; even the *Cal. Blumenbachii* of Gothland limestone is not wanting. The constituents of that rock are however principally black slate, with subordinate limestone and likewise black. This homogeneity of the deposits renders the separation of the respective subdivisions more difficult there than in the other parts of Northern Europe.

The above formations are covered in Russia by a second powerful rock formation, which constitutes the Waldai plateau; thence extending itself to the extreme North of Europe. It is composed of sand and sandstone, corresponding with the old red of English geologists, and of a limestone abounding in *Producta* and *Spirifera*, viz. mountain or carboniferous limestone. Two species of tails of Trilobites are met with in the latter, *Asaphus Eichwaldi* and *Brongniarti*, Fisch. v. Waldh.; they correspond exactly with caudal shields of *Griffithides* and *Phillipsia*, Portl., which are likewise peculiar to the mountain limestone in England.

2. *British Islands.*—The British palæozoic rocks have still more members than those of Northern Europe. In addition to this it must be stated that the relations of strata are not so readily apparent or striking; its strata are arranged either in lines or in centres of elevation, and are partially changed by the influence of plutonic rocks. Taking these various causes into consideration, it cannot surprise us that only the most strenuous

endeavours of Murchison and Sedgwick succeeded within a few years in throwing light upon this chaos. Murchison divides at present the English palæozoic rocks into two systems,—the *Silurian* in the West (compare Murchison's 'Silurian System,' London, 1839), and the *Devonian* in the South-west of England. The first he again classifies into two principal divisions and seven separate members. We first of all meet with, situated upon the lowest slates, void of fossils (upon the Cambrian system),—1, the Llandeilo flags, a formation resembling the grauwacke, generally calcareous, traversed by veins of calcspar, and containing mica, in which formation whole strata are filled with *Ogygia Buchii*; in its company occur the northern *Battus pisiformis* and *Illænus perovalis*, which I cannot distinguish from *I. crassicauda*. *As. tyrannus* very much approximates to *A. angustifrons*. *Trinuclei* are numerous. Llandeilo in South Wales (Caermarthenshire) is the classic district where this member most abounds in fossils. Upon this follows,—

2. *The Caradoc Sandstone* *. Abounding in *Trinuclei*, of which two occur in the Llandeilo flag (*T. Caractaci* and *fimbriatus*). The *Ill. perovalis* also occurs again in this. *Phacops Powisii* is the *Phacops sclerops* of the North. It cannot be proved from a mere caudal shield whether *Calymene punctata* corresponds with the species of Gothland, since this form of it is found in several species.

3. *Wenlock shale*, a slate poor in Trilobites, and corresponding in that respect with the next member; it contains *Ph. caudatus* and *mucronatus*; the latter, however, is wanting in the limestone.

4. *The Wenlock limestone*, on the other hand, has been a favourite locality for Trilobites for ages. The Dudley fossil bears the name of the principal place for Wenlock fossils, and has carried the name of the picturesquely-situated Dudley through the world. Besides this fossil, the *Cal. Blumenbachii*, it is known to contain *Phacops Downingiæ, macrophthalmus, variolaris, caudatus* (incl. *tuberculato-caudatus*), *Odontopleura Brightii, bimucronata* (*Parad.*), Murch., *quadrimucronata* (*Parad.*). *Brontes flabellifer* and *Homalonotus delphinocephalus* are likewise enumerated among the Wenlock fossils; I should suppose, however,

* Called *Caradoc* from a hilly range bearing this name in South Shropshire: the name is derived from Caractacus, the celebrated British chieftain, who waged war with the Romans.—*Tacit. Annal.* xii. 37.

that they are rare, for I have not met with a trace of them on the numerous Dudley flags which I have had an opportunity of examining. It by no means appears clearly established from Murchison's work that *Bumastus Barriensis* really belongs to this formation; it is very possible that the strata in which it is found belong to an older formation. Not one of the fifteen species which Murchison enumerates has as yet been found in the Llandeilo flags and in the Caradoc sandstone; we meet, however, with several of them in the next following subdivisions.

These, 5. the *lower*, and 7. the *upper Ludlow slate*, which are separated from one another by 6. *Aymestry limestone*, a blue limestone of little thickness, contain only few Trilobites. We certainly still find here in the lower and central strata the *Calymene Blumenbachii* and the *Phacops caudatus*; but as its real characteristic we can only adduce the genus *Homalonotus*, one species of which, *H. Knightii*, is stated to occur widely distributed in the upper strata; *H. Ludensis*, on the other hand, seems to be more rare. *H. delphinocephalus* occurs both in the lower strata and in the Wenlock limestone.

In order to compare the English with the northern strata, we require above everything some characteristic from which we may ascertain the relative age, upwards and downwards, of the respective strata. The comparison of the limestone of Gothland with that of Dudley presents such to us without any difficulty. The similarity of both is striking. I will pass over the numerous corals, which occur in both localities of equal beauty and frequency; they possess too great a vertical extension to enable us to solve this question. The similarity, however, is likewise equally great with respect to other families. Of Trilobites, we find in both localities *Phacops caudatus*, *variolaris* (which M. Kranz brought from Klintehamm in Gothland), *Blumenbachii*: species which are wanting in the lower strata of both countries. The only Gothland Trilobite which is enumerated from the lower Silurian strata of England is *Cal. punctata*, which, from the reason just mentioned, cannot decide the question. The similarity is still more striking in the Brachiopoda, *Terebratula Wilsoni*, Sow., *borealis*, V. B., *marginalis*, Dalm., *cuneata*, Dalm., *bidentata*, His., *didyma*, Dalm., *reticularis*, Wahlb., var. *aspera*, Schl.; *Spirifer cardiospermiformis*, Dalm., *crispus*, Dalm., *trapezoidalis*, Dalm.; *Leptæna euglypha*, Dalm., *depressa*, Dalm., *transversalis*, Dalm.; all of which occur in the Dudley

and Gothland limestone, and therefore sufficiently prove the similarity of both.

The Trilobites likewise present some, although not numerous, points of comparison between the lower Silurian formations of England (1 and 2) and the lower strata of the Swedish rocks (1—3). *Illænus perovalis* is certainly a young *Ill. crassicauda*; *Phacops Powisii* (the caudal shield represented with it does not belong to it, as Capt. Portlock correctly observed) is identical with *Ph. sclerops* of Sweden and Russia. *As. tyrannus* is a species of the genus *Asaphus*, Brong. *emend.*, highly characteristic for the lower system of strata of the Baltic countries. But it cannot be denied, that the dearth of genuine *Asaphi*, which are contained in such numbers together with the English *Trinuclei* in the northern system, not far remote from it, is a remarkable feature. Of *Orthis* we also again meet with some of the most remarkable Baltic forms in England; I allude to *O. callactis*, Dalm., and above all to the very singular form of *O. anomala*, Schl.; they occur in the Llandeilo and Caradoc formation. All these forms are met with in the two lowest members of the English Silurian rocks and the principal limestone (2) of Sweden and Russia.

Such an identity, however, as is found between the Wenlock and Gothland limestone is entirely foreign to the subdivisions we have last contemplated; the character of the rock is entirely different, and with it also the zoological character. The trifling development of the family of the *Orthoceratites*, which are found at certain localities of the northern limestone in surprising numbers, is a more remarkable circumstance in this respect than any other. Of the fossils of the northern alum-slate, the *Paradoxides* slate, England possesses only the *Agnostus pisiformis* in the lowest strata, viz. the Llandeilo flags. The Llandeilo flags and the Caradoc sandstone correspond therefore with the Trilobite and Orthoceratite limestone of Sweden and Russia, perhaps including the *Paradoxides* slate. The slate of West Gothland accordingly meets with its equivalent in the Wenlock shale (the prevalent Trilobite in both is the *Ph. mucronatus*), and the Gothland limestone meets with its equivalent in the limestone of Wenlock. The higher members are scarcely represented in the North. We have now still to consider two formations in England containing Trilobites, viz. the transition rock of Devon in the south-west, and of York in the north-east; we are acquainted with the Trilobites of both through the work of Prof. Phillips

(Palæozoic Fossils, London, 1842, and Geology of Yorkshire, vol. ii.).

A thick sandstone and conglomerate formation, the old red, deposited in the West and North of England, on the transition rocks described, is extremely poor in fossils; the mountain limestone, on the other hand, which separates this old red sandstone from the coal formation in the more restricted sense, abounds with them. Amidst an abundance of *Producta*, *Spirifera*, *Terebratula* and *Crinoidea*, some few Trilobites, certainly for the greater part in a mutilated state, are also hidden, the last lingering representatives of this interesting family. Portlock formed for their reception the genera *Phillipsia* and *Griffithides*, which have already been mentioned when treating of the mountain limestone of Russia.

The coal formation is likewise found to be deposited, although in a heterogeneous manner, upon the lowest fossiliferous rocks. The plants of the former correspond exactly with those of the true coal formation; a subordinate black limestone likewise contains two Goniatites of the mountain limestone (*G. miscolobus* and *crenistria*). It can of course not be my intention here to treat minutely of the geology of Devon; suffice it to say, that we find there a very considerable transition formation, resting upon a crystalline rock, overtopped heterogeneously by coal formation, its lowest member consisting of clay-slate, its upper of a red sandstone slate (grauwacke), with which are interspersed several limestones distinguishable by their fossils. Whilst only few fossils of the upper Silurian group re-occur in the true mountain limestone, there is, on the other hand, a remarkable occurrence of the peculiar animals of both formations simultaneously with new ones. Phillips found one-tenth of Silurian, one-fifth of mountain limestone species; the remaining seven-tenths he declares to be peculiar to these Devonshire strata. It is not without reason that we presume that a less acute determiner of species than Mr. Phillips would have detected a considerably greater number of carboniferous limestone and Silurian species among them. But even the facts enumerated justify the assumption of Phillips and Murchison, that the transition rock of Devon is an intermediate formation between the Silurian formation and mountain limestone, an equivalent of the old red sandstone formed at the same time in other parts of England.

According to Mr. Phillips, the Trilobites belonging to this

Devonian system of stratification differ entirely from the Trilobites of the other English strata, excepting only *Cal. Latreillii* and *granulata* (*Phacops macrophthalmus*). It contains *Cal. accipitrina, lævis, granulata, Latreillii* (species of *Phacops*), *Sternbergii, Harpes macrocephalus, Asaphus granuliferus, Brontes flabellifer*, and other species of this genus. Of all these, the two species, *Ph. macrophthalmus* and *Brontes flabellifer*, already occur, although rarely, in the Wenlock limestone; one species, *As. granuliferus*, on the other hand, is a Trilobite of the mountain limestone, whilst the very remarkable *Cal. Sternbergii* and *Harpes* are, together with the others, genuine Devonian Trilobites. The distribution of the Trilobites confirms, therefore, as well as that of other fossil animals, the separation of the transition rock into four principal subdivisions; into a *lower* and *upper Silurian*, into a *Devonian system*, and into *mountain limestone*. They may all be characterized by species, and even by genera of Trilobites peculiar to them. But however distinctly these subdivisions differ from one another by the nature of their constituent rocks and fossils, this is not the case even on *British* soil—everywhere. The fact of a rock of an entirely different character being deposited from the ocean in the south-western part of the present country, pretty nearly at the same period with the red conglomerate and sandstone formation in the west and north-west of England, is in favour of the view that local influences were not excluded during the formation of the palæozoic rocks. Conglomerate formations naturally possess the most local character of all rocks deposited from water; clay formations, and next to them fine granular sandstone formations the most general. Limestones hold an intermediate rank; they are frequently wanting under circumstances that admit of no possibility of a previous destruction of them. I allude to Sweden and Norway. The English transition formation exhibits a similar relation to that of the neighbouring island of Ireland. The transition rock in the northern part of this island, in the county of Tyrone (compare Portlock's 'Geology of Londonderry,' 1843), projects in two small districts from amidst the old red sandstone; these two districts are in the parishes of Pomeroy and Desserlcreal in the vicinity of Dungannon. Both are formed of grauwacke slate which resembles very much the Caradoc sandstone; limestone deposits are wanting; the stratification is dis-

turbed in the highest degree. It is owing to these causes that it has hitherto been impossible to separate it into subdivisions. The fossils, which Portlock describes and figures from these strata, evidently belong to the three lower systems of the transition rocks, to the two Silurian and to the Devonian. To confine ourselves, however, to the Trilobites, Portlock enumerates the following belonging here:—1st, *Trinuclei*, of the Caradoc sandstone (*T. Caractaci* and *radiatus*), *Asaphi*, of the lower northern limestone, North American *Isotelus*, in company with Swedish *Illænæ* (*I. crassicauda* and *centrotus*); to these we must add, 2ndly, *Calymene*, of the upper Silurian formations (*C. Blumenbachii, C. pulchella*); and finally, 3rdly, the Devonian genera *Harpes*, *Brontes*, and *Arges*, in beautifully distinct species. Besides these we find representatives of the North American genus *Nuttainia*, and splendid new species of *Encrinus*, *Phacops*, &c. This occurrence of Trilobites is, therefore, in a double point of view, the most interesting with which I am acquainted; in one respect, on account of the concentration of the Trilobites of all formations over so small a space, and because they occur in a homogeneous rock. The latter circumstance favours the conjecture of the same external conditions of life having continued for a long period, and readily accounts for the fact that Trilobites of different formations are here united in the same stratum. It is hardly possible, however, that all these genera of Trilobites lived there at one and the same period. It is equally interesting on account of the association of northern forms, especially of Trilobites with British forms. Species common to both the Scandinavian and English transition rock are rare; they are more numerous in the Irish transition rock. That this is the only spot in Europe where the inhabitants of the earliest North American oceans are found mixed with the European, may perhaps have its origin in the currents; indeed, even the most recent organic formations of the present day about Ireland would show to us a similar relation, for the ocean on the west coast of Ireland daily washes on shore American produce.

The mountain limestone of Ireland, of Kildare, Cork, &c., which abounds in Trilobites, on the other hand exhibits the normal character, the same succession of strata, and the same quality of rock as in England. It is separated from the transition rock by the old red sandstone, and covered by the true coal forma-

tion. It contains other crustaceous remains besides the *Phillipsia* and *Griffithides*, which approach to the orders of the genuine *Pœcilopoda* and *Phyllopoda*, viz. *Limulus* and *Dithyrocaris*.

3. *France.*—France, notwithstanding the extent of the transition formation, is a country poor in its fossils. This may be owing to the predominance of the clay-slate. The whole mountainous north-west of the country, Normandy, Bretagne, and the district on the lower Loire, consists of it for the greater part. The occurrence of *Ogygia Guettardi* and *Desmaresti* at Angers is well known, likewise that of the *Cal. Tristani* in the Cotentin; less so that of the English *Trinuclei* (*T. Caractaci*) at Ste. Bregitte in Normandy in a clay-slate which contains Chiastolite: all of these slates most probably belong to the lower Silurian system. Besides the Trilobites mentioned, I only further know of a *Homalonotus* from the red sandstone of Caen, an evidently younger link of the upper Silurian system.

4. *Germany.*—The palæozoic rocks occur here over a very considerable extent at five localities. Of these, the large plateau of the Lower Rhine occupies the first place; uniformly resting on its undulating ridge, abounding in picturesque valleys, of which many deserve to hold an equal rank with the celebrated "Valley of the Rhine," it extends at an average level above the ocean from the Sambre in Belgium to the Diemel in the west, accompanied towards the north and south by the richest coal formation of the continent (Valenciennes, Namur, Liège, Eschweiler, Essen, in the north; Saarbrücken in the south). Both transition and coal formation contain Trilobites as widely diffused as in those of England. The plateau of the Voigtland is far inferior to the former in extent; it, nevertheless, extends from Bless near Schalkau to the neighbourhood of Freiberg, and from Gera on the Elster to the crystalline slates of the Fichtel mountains. The grauwacke and clay-slate plateau of the Hartz, which island-like elevates itself from the younger surrounding formations, is of still less extent. The fourth German locality is in the interior of the Bohemian basin; it occupies a triangle like the preceding one, which extends from Prague to near Klattau, and is turned with its western side towards the Bohemian Forest. It bears in its centre the somewhat considerable coal measures of Bohemia. Finally, of the fifth, or *Upper Silesian-Moravian* Grauwacke system, we know but too few Trilobites to render it worthy of particular notice. Upper Si-

lesia, on the other hand, possesses another remarkable Trilobite locality of Germany, in addition to its northern specimens, in the so-called grauwacke of Falkenberg, a member of the carboniferous formation of the coal system.

Of the enumerated grauwacke systems of Germany, probably none exceeds that of Bohemia in point of age. Between Beraun and Pilsen, in a generally darkly coloured grauwacke, we find the *Oleni* (*O. Tessini, spinulosus*), which hitherto have not been found anywhere excepting in Sweden and in North America. *Conocephalus* and *Ellipsocephalus* are peculiar to this formation. It can only be decided at the locality itself whether the more yellow rock, in which *Phacops proavius* (a species most nearly related to *Ph. Downingiæ*) occurs, belongs to the same grauwacke, or to a younger. Count Sternberg makes mention of a lighter grauwacke, which appears to the north of the former, and accompanies the coal formation. Older limestones, subordinate to the grauwacke, and containing fossils, are not known. A range of young transition limestones commences on the other hand at Prague, and extends from Karlstein to the vicinity of Zebrak. It abounds in Trilobites: we know from it *Phacops macrophthalmus, protuberans, Hausmanni, Trilobites Sternbergii*, and some small remains which require to be more accurately investigated, and from which Zenker formed the genus *Otarion*. What are not peculiar to Bohemia occur in the Devonian strata of England (*Ph. macrophthalmus, Calymene Sternbergii*).

I am not acquainted with any Trilobites from the grauwacke and clay-slate of the plateau of Voigtland; the fossils found there however do not lead us to expect the discovery of the Bohemian *Oleni*. The limestones of the Fichtel Mountains, on the other hand, are richer in fossils in the vicinity of Hof. Among the numerous fossils which Count Münster discovered in them are also Trilobites: species of *Brontes, Calymene Sternbergii*, different species of *Phacops*, with a large trapezoidal lobe of the forehead, and with an evanescent small lobe of the forehead (*Ph. granulata, intermedia, lævis*, Münster, *Latreillii*, Stein.). The *Bumasti* and *Illænæ* have been found in too imperfect a condition to deserve any consideration. All the Trilobites that admit of being determined correspond with those of Branik and Karlstein, as well as with those of Devonshire.

The Trilobites of the Hartz are known from Rœmer's work on the Fossils of the Hartz (Hanover, 1843). He represented

from the grauwacke the *Homalonotus Ahrendi*, which I cannot distinguish from *H. Knightii*. Neither description nor figure shows with any degree of certainty whether *Calymene Jordani* is a species already described or a new one. It sufficiently appears, however, from the figure to belong to the division of the *contractile* species of *Phacops* with lateral lobes of the forehead, which has hitherto only been known from the Silurian system, but both from the lower as well as from the upper divisions. The Hartz can therefore only be proved from the Trilobites to possess the upper Silurian group; neither the Trilobites nor any other fossils that have hitherto been found there are sufficient to support Dr. Rœmer's rather precipitate assertion that all the subdivisions of the English Silurian system are again met with in the Hartz. It is certainly possible, but cannot yet be proved. We likewise are only acquainted with very few animal remains of this order from the beds on the dip side of the grauwacke of the Hartz; we may however infer a Devonian formation from the caudal shields of *Brontes*, which were found in the limestone (abounding in fossils) of the Winterberg near Grund, and from that of the Scheerensteig in the valley of the Selke; and the other fossils found there also favour this supposition.

Want of space, I regret to say, necessarily limits me to a few remarks on the most subdivided of the German transition rocks, and which most abound in Trilobites, those of the Lower Rhine. Grauwacke and grauwacke-slate likewise predominate here; they contain *Homalonoti* (*Knightii, Herschelii*) and *Calymenæ*; it still requires further confirmation whether the true *C. Blumenbachii*, which Murchison enumerates, occurs among them. The Eifel limestone is more important, indeed the most important, of the German Trilobite deposits. It is superposed in several isolated hills, saddle-like, on the grauwacke, surrounded entirely by the latter, and partially projecting above it in the form of high rocky cliffs. Gerolstein and Blankenheim are the principal localities of the numerous and interesting Trilobites described by Professor Goldfuss. From these localities are *Phacops arachnoides*, Goldf., *macrophthalmus*, Brong. (which are particularly numerous), *Harpes macrocephalus*, G., *Brontes flabellifer*, G., *Gerastos*, and others. Some of them are peculiar to the Eifel, at least they have not yet been found anywhere else; others however also occur in Devonshire (*Harpes, Brontes, Phacops macrophthalmus*) in association with other characteristic Eifel fossils

(*Calceola*, &c.). These have also been met with in the other German transition limestones. It is remarkable that none of the Eifel Trilobites of the palæozoic rocks have as yet been met with on the right shore, with the sole exception of *Ph. macrophthalmus*. Of this species I only know two places on the right shore where they are found, Cromford in the north, (south-west of Elberfeld), and the roofing-slate of Wissenbach near Dillenburg. This slate follows immediately upon a grauwacke containing *Homalonotus*, being itself overtopped by a limestone containing Eifel fossils, but without Trilobites, and separated by a second, more earthy slate formation, the *Posidonomya* slates of Herborn. The *Calym. æqualis*, evidently allied to the genus *Phillipsia*, favours considerably the referring the Herborn slate to the lower coal formation. Dr. Beyrich discovered the frequently mentioned facetted-eye *Phacops* (*cryptophthalmus*, perhaps identical with the Devonian *lævis*) in the goniatite limestone of Obenscheld, likewise near Dillenburg. The same species is found in the Cytherine slate not far from Weilburg, according to a specimen with which I was kindly made acquainted by M. Althaus. The last Rhenish deposit of Trilobites known to me, is that occurring in a white genuine mountain or carboniferous limestone at Ratingen, abounding in *Productæ*. The *As. Dalmani*, G., confirms likewise in the present instance the regular distribution of the Trilobites in the series of strata; it also belongs to the genus *Phillipsia*, peculiar to the mountain limestone. The same fact is also confirmed by the last German locality of Trilobites worthy of remark, viz. the Falkenberg deposit resembling grauwacke in the county of Glatz. The *Griffithides obsoletus*, Phill., of the mountain limestone of York occurs here, associated with numerous *Productæ*; the caudal shield of another Trilobite found in this deposit belongs to the same genus, or to *Phillipsia*.

If, in conclusion, we draw in all briefness the final result accruing from the above researches on the distribution of the Trilobites in the European strata of rocks, we arrive at the conviction that there is scarcely any other family of the animal creation more calculated than that of the Trilobites for the characterisation and determination of the various members of the palæozoic rocks. The ease with which the species and genera are distinguished by striking characters, and their slight vertical extension in the strata, which, on the other hand, is very great in

a horizontal direction, render them peculiarly adapted for this purpose. They moreover prove that the species of fossil animals likewise constitute distinct individual groups, that no species can be derived from another, that no metamorphosis and progressive development of one form into another can have taken place. We certainly cannot conceive of a repeated origin of new species, a continual act of creation; but let us ask ourselves, is the very first appearance of animal life on our earth more comprehensible to us? This has always been an enigma to the human understanding and to human science, and will always remain so; the constantly recurring production of new forms of animals and plants that had never previously existence forms a parallel to it.

Article XII.

On the Employment of Polarized Light in studying various questions of Chemical Mechanics. By M. Biot*.

[From the *Annales de Chimie*, t. x., 1844.]

Section I.—*General considerations which serve as bases for the theoretical formulæ applicable to this class of experiments.*

1. HAVING seen, in the Proceedings of the Academy of Berlin, that Professor Mitscherlich has entered upon the investigation of the molecular actions exercised upon polarized light by saccharine substances, as well as by tartaric acid in its various states of combination, and being persuaded that so inventive a philosopher having once entered upon this path of investigation cannot fail to reap a rich harvest of discoveries, it has occurred to me that I might still, with advantage, remove some of the difficulties of detail which are here met with, and show the extent of the theoretic deductions which may be derived from it, by stating the unexpected results to which it has led me respecting the internal state of liquid systems, in which several bodies, placed in contact, react invisibly upon each other, by their reciprocal affinities, without being mutually decomposed. These results, in the most simple cases, follow from the experiments already recorded in the *Mémoires de l'Académie des Sciences*, particularly in vols. ii. xiii. xv. xvi., as well as in the *Comptes Rendus* of the Academy, which have been published subsequently. I shall complete them here by several series of observations made during the summers of 1835, 1836 and 1837, on liquid systems formed by tartaric acid, boracic acid, and water, at constant temperatures, varying in each series the relative proportions of the three bodies, in every degree compatible with the state of liquidity. The effects produced on polarized light by these systems have been observed, in each case, with every proportion of boracic acid which could be successively introduced; and they have been found capable of being connected by the same form of numerical law which systems less complex, or

* [The editor is indebted to the Rev. Prof. Lloyd, F.R.S., &c. of Trinity College, Dublin, for his kind assistance in revising the translation of this memoir.]

studied under more simple circumstances, had previously presented to me. The existence of such laws was not improbable, considering the almost immaterial sensibility of the agent employed; and the hope of discovering them alone led me to persevere in the laborious task which their investigation required.

2. I may be allowed to indicate here one of the points of view under which this kind of experiments seems to offer the greatest utility to science, and under which I propose to regard it specially in what follows. Experimental chemistry is at present very rich in complex facts; but these facts presenting, for the most part, only reactions already complete, throw no light upon the previous physical state of the material systems in which they are produced, any more than upon the mechanism of the molecular forces which determine them. This twofold knowledge would however be indispensable to connect hereafter chemical phænomena with strict mechanical theories, just as the movements of the planets and capillary phænomena have been reduced to similar theories, by deducing the first from attraction varying inversely as the square of the distances, and the latter from attractive forces becoming insensible at sensible distances, in which respect they are analogous to affinities. We might, at the first view, hope to find bases on which to rest such calculations, in the succession of definite products, proceeding by multiples of simple proportions, which the same material substances form on combining one with another, under various circumstances. But although this important remark is extremely useful to practical chemistry, to decide the formation of these multiple combinations, and even to predict, in many cases, their possibility, it offers no hold for mechanical calculus; first, because the diversity of circumstances may have essentially modified the individual constitution of the combined substances, or that of the product resulting from their reaction, by changing the absolute quantity of imponderable heat which forms a part of it, that which would alter the supposed identity; and secondly, because, even admitting this scarcely probable identity, calculation, which can be established generally only upon continuous data, could not deduce the forces from such intermittences, except by connecting them by ideal conceptions supported only by isolated verifications; and the chance of ascertaining in this manner the general mechanism of the reactions would be single, whilst the chance of error would be infinite. Thus, notwithstanding the importance of such a problem, no geometrician has hitherto

ventured upon it; and in fact I do not hesitate to say, that, thus regarded, it could not have been solved. For the experiments which I shall relate will prove that definite combinations, proceeding by intermittent proportions of simple multiples, are wholly exceptional cases in the series of chemical reactions; that they are isolated, so to speak, from the continuity of those reactions by the intervention of forces or of circumstances which interrupt that continuity. So that, to endeavour to ascend from thence to the general mechanism of the material systems from which these intermittent combinations are separated, or which are transformed into them by a sudden convulsion of all their parts, would be to place ourselves in a more unfavourable position than that of the geometrician who should seek to deduce the nature of a curve or of a surface from the mere knowledge of its individual points, without any notion of the general conditions which characterize the continuity of its course. Now it is this character of continuity which I proceed to establish in the phænomena I propose to consider.

3. For this purpose, conformably to all physical and chemical inductions, I shall consider bodies permanent, of sensible dimension, as composed of disjointed particles, having, in their inappreciable minuteness, individual configurations and properties, and kept at a distance by forces of whose nature we are ignorant, but whose existence is manifested by the property which all sensible masses have of contractibility and dilatation, within certain limits, without decomposition. Taking, then, such a system in the state of relative mobility of its parts which characterizes perfect fluidity, I shall apply to it a principle which may be established by mathematical demonstration, and verified in all its deductions by experiment; the following is the proposition.

When a perfect liquid, physically homogeneous and of uniform temperature, being traversed perpendicularly by a ray polarized in a given plane, impresses on the plane of polarization of this ray deviations of constant direction, which preserve the same direction and the same amount, in the relative state of agitation or of repose of the particles, such an effect could only be produced mechanically by an action which the *geometrical* elements of the liquid mass would exercise, in all directions, with an equal energy. Its dissymmetry around the normal can only result from a molecular power peculiar to the imagined material groups which constitute this mass,—whether this power

emanates individually from all, if the liquid is chemically homogeneous, or only from a certain number of them, distributed uniformly among the others, if it is not. This proposition will be sufficiently evident to geometricians, by the very symmetry which I have just expressed. It is verified experimentally in all its physical consequences by a multitude of results, one of the most evident of which is the exact proportionality observed between various thicknesses of one and the same active liquid, and the magnitude of the total deviations which it impresses on the plane of polarization of the same luminous ray, whether employed in continuous or discontinuous columns. The identity of the ray is necessary, because the effect produced is generally unequal on rays of different refrangibilities. In all diaphanous liquids hitherto observed, with the exception of those of which tartaric acid is one of the elements, the deviations produced by one and the same thickness in the planes of polarization of different simple rays are very nearly, although not exactly, reciprocal to the squares of the lengths of their *fits*, which renders them relatively stronger for the most refrangible rays. But in liquids of which tartaric acid forms a part, especially where it is not very intimately combined with other bodies, the dispersion of the planes of polarization follows wholly different laws, which may even be varied almost at will by modifying the temperature of the system, or the proportion of its elements, or the nature of the substances in contact with the acid.

4. The permanence of the optical action exercised by the liquid masses in a state of repose, as well as of relative mobility of their particles, which is a fundamental condition of the preceding principle, is verified, so to speak, without preparation, in the natural state in which perfectly fluid masses are observed. For we may very well presume that, in the midst of the external circumstances by which they are surrounded, the particles composing them are as little fixed as those of gases. But we may prove this fundamental fact by means of the following apparatus. In a large tube terminated by thin glasses with parallel faces, I inserted laterally a metallic rod, bearing at its inner extremity a plane metallic diaphragm, having in its centre an annular opening; so that on turning this rod in various directions, by its projecting extremity, I was able suddenly to agitate the liquid with which the tube was filled. But these

movements produced no appreciable change in the total deviations which its mass impressed on the planes of polarization of the luminous rays. The effect was still the same, and as constant, when a clock movement was applied to the rod, which caused the diaphragm to turn with such velocity that its periodical passage in the plane of the eye was not perceptible; so that there was no perceptible intermittence in the continuity of the sensation *. Moreover, this artificial agitation, although so quick, was yet perhaps very slow in comparison to the internal vibrations which the molecules of liquid, and even of solid bodies, execute, without doubt, spontaneously either amongst themselves, or around their centre of gravity in their usual state, under the influence of opposite forces which attract them to one another, and which keep them at a distance; for in such circumstances the case of an exact and permanent equilibrium would be altogether exceptional.

5. The preceding experiment was successfully made upon cane-sugar syrup, which possessed a very perceptible viscosity. But the molecular character of the action may likewise be made manifest in systems completely viscous, whose sensible parts possess relatively too little mobility for the same process of mechanical deplacement to be applied. Such, for example, are the semi-fluid secretions of the *Coniferæ* and the *Terebinthaceæ*, commonly known under the general name of turpentines. If we take these substances as they are found in commerce, and purify them by filtration in a water-bath, or in a warm chamber at a moderate temperature, we obtain products which are still viscous and more or less coloured, but very limpid, and which act upon polarized light in different directions as well as different intensities, according to their origin and the preparations which they have undergone; this proves that they are of very different natures †. All these products coagulate by repose and with a

* *Comptes Rendus des Séances de l'Académie des Sciences*, t. xvii. p. 1209.

† I formerly had at my disposal similar products, which all impressed on polarized light deviations toward the left, as the pure essence of turpentine. The first time that I found one exercising right-handed deviation, I was very much astonished, and I begged M. Soubeiran, who had had the kindness to purify it by filtration, to submit it again to distillation, in order to extract the essence. He did this in two ways; by distilling it with water, and without water. Now, to our mutual surprise, the two volatile liquids thus obtained exercised the deviation *toward the left* with different energies, and both much less than that of the pure essence of turpentine; so that they were dissimilar among

slight refrigeration; so that the bottle containing them may be reversed without their being detached, and even without the action of their own weight disuniting their mass, except after a certain time, proportioned to the lowness of the temperature. Nevertheless, under these circumstances, where the *sensible* elements of the total mass can continue to receive only very slow and very crampt relative movements, we may still perceive that the action exerted upon the polarized light is molecular, and independent of the occasional aggregation which the approximation of the elements has caused them to contract. For in the first place, for the same mass, this action has the same direction as in the liquid state. In the next place it has an energy differing little for equal thickness; and lastly (a fact which is decisive), its total effect is always proportional to this thickness, whatever be the internal direction of the transmitted ray. These characters may be easily verified, if not with complete accuracy, at least with an evident approximation, by receiving immediately the filtered products into flasks sensibly cylindrical, through which they are observed while they are still liquid, and again after they are coagulated. For, in this latter state, as in the first, if the flask is turned around its axis, so that the polarized ray traverses it successively by its different diameters, the deviation observed remains constant in direction, as in amplitude, with the exception of some small variations which may be produced in this amplitude by the inequalities of the internal diameters; and through flasks of unequal size the deviation impressed by the same substance on the same type ray is propor-

themselves and with the latter, as their odour equally indicated. The deviations observed by the naked eye, through a thickness of $99^{mm}\cdot5$, were, for the essence obtained by distillation with water, $-7°$ ←; for the essence derived by distillation without water, $-19°$ ←; whilst the pure essence of turpentine, observed under the same circumstances, exercised a deviation equal to $-34° \frac{1}{2}$. The matter observed originally was therefore a compound which was destroyed by distillation, either by removing the essences from it, or determining their formation. Various analogous products, known in commerce under the name of Swiss turpentine, also presented to us right-handed deviations; but that which is extracted from *Pinus sylvestris* exercises a deviation toward the left, to judge by a specimen from that species which has been given me by M. Dubail. It would be interesting to extend these chemical and optical tests to the different products thus obtained, if we could procure them from certain sources, and M. Soubeiran proposes to take an opportunity of doing this. This study might above all be undertaken with advantage by chemists residing in the very places where these kinds of substances are obtained, because they could then determine the variations of their nature, not only for the different species of trees, but for the same species in its different parts, at different seasons of the year, and at the different periods of its life.

tional to their mean diameter. To effect this test with complete exactness, boxes of a rectangular or cubical form should be constructed, the sides of which are of thin glass with parallel faces, the upper one of which may be removed and replaced at will, the fixity of their apposition being moreover secured by metallic bars attached with screws. After having measured exactly the inner interval of the glasses in various directions in which they are opposed, the flask, containing the filtered and viscous turpentine to be tested, is slowly heated in a water-bath, gradually to boiling. When it is thus brought to an entire state of liquefaction, which renders it completely homogeneous, it is poured gently into the hot box, avoiding the formation of internal bubbles of air, or waiting till they are disengaged: the upper glass is then replaced, which is perforated with a circular orifice, through which the excess of the liquid escapes; and, after the mass is coagulated by spontaneous cooling, the upper glass, which the viscosity of the matter has already rendered adherent, is fixed by the metallic bars. We thus obtain a limpid homogeneous mass, of known dimension and of uniform constitution, except around the orifice, where the contraction caused by the cooling produces an empty space, which is filled with air. But this, far from being an inconvenience, is an advantage, because the regularity of the constitution of the medium is not at all interfered with when the observation is made at some distance from the empty bubble, and a space is left, in which the matter may extend freely, if it be desired to raise it anew by heat to progressively higher temperatures, or even to complete liquefaction, in order to observe it in this state without changing its dimensions. I shall hereafter recur to the modifications which this diversity of temperature produces in the optical effects. For the present I limit myself to the consideration of those which are obtained when the inclosed matter is in a state of coagulation. In this case, if a homogeneous ray is transmitted, not only under the normal incidence, but under any equal incidence whatever, through the various pairs of parallel faces of the apparatus, the deviations produced in its plane of polarization are equal among themselves in the cubic case, and proportional to the lengths of the course in the rectangular case, whatever parts of the mass be traversed, and whatever be the directions in which the transmission is effected; provided always that the observation be made at a sufficient distance from the limits of the empty

bubble, where the surfaces of the acting substance are curved by capillary action; and supposing also that the feeble portion of light is neglected which may be depolarized, or polarized in a different direction, by the ordinary refraction at its entrance and emergence, if the plane of introduction were oblique to the plane of primitive polarization*. With these exceptions, the experiment therefore proves that the internal mass is constituted symmetrically around each of these geometric points; and consequently the dissymmetrical effect undergone by the ray, around its plane of primitive polarization, cannot result from such a state, but from the individual action of the insensible particles which compose this mass. Similar characters demonstrate the existence, or rather the persistence of the same molecular action in certain media brought to a state of perfect solidity. But in this case it becomes observable only under certain conditions, which I shall indicate hereafter; and I shall then relate, as examples, cases in which it is established by these processes.

* The homogeneity of the transmitted ray is obtained with sufficient exactness by receiving it through certain glasses coloured red by protoxide of copper, in which this property has been previously ascertained by analysis with a prism. But for comparative determinations, like those under consideration, the experiment may be advantageously facilitated either by measuring the deviations by the naked eye, if the medium observed is colourless, and taking for type the extraordinary tint of bluish-violet, which is always manifested in comparable azimuths, except in solutions of tartaric acid; or, if the medium is coloured, by equalizing its tints in different directions by the interposition of a glass of an analogous, but somewhat darker tint, as I have explained in the *Comptes Rendus des Séances de l'Académie des Sciences*, t. xv. p. 624 and 632. I have recently applied the first process to the observation of a variety of turpentine, which produced a deviation toward the right. The dimensions of the bottom of the case which contained it were 90 millimetres and 50 millimetres; its height 49 millimetres. The deviations in these three directions were observed by the naked eye, and determined by the azimuth of the evanescent bluish-violet tint, the unfavourable state of the weather not allowing conveniently the employment of a coloured glass. On reducing them to the true zero of the apparatus, that is to say to the observed plane of polarization of the primitive ray, they were found to be respectively $+ 35°{\cdot}50$; $+ 21°{\cdot}00$; $+ 20°{\cdot}50$. To compare their relations to what they ought to be, in the condition of proportionality, I form their total sum and that of the corresponding dimensions, which gives 77° of mean deviation for a total thickness of 189^{mm}. Then, deducting the partial deviations from this mean result, according to the respective thicknesses, we find $36°{\cdot}67$; $20°{\cdot}37$; $19°{\cdot}96$, that is to say, the first a little higher and the two last a little lower than they were found by observation. Now this apparent difference only confirms still more the law of proportionality, *which applies to one and the same simple ray*; for the substance observed being sensibly coloured greenish-yellow, the transmitted ray lost a much greater proportion of its most refrangible, and consequently most deviable elements, through the long dimension of the apparatus, than through the two smaller ones; so that the first deviation should be greater than the observed, and the two last lower, when all three are calculated according to the mean sum of their observed values.

6. Now, it may be asked how material particles should be constituted to produce thus a total effect sensibly constant, in all the relative positions which a mechanical agitation imparts to them when they are altogether liquid, and in those probably not less variable which result from their internal vibrations, when they compose a coagulated or solid mass, the parts of which appear to be in repose relative to our gross senses? It is easy to form a conception of this, if not absolutely certain, at least mechanically admissible, without framing any hypothesis on the nature of light. It suffices for this to transfer to the constituent molecules of the active masses the same properties which these masses present to us, and which we see to be in them independent of their accidental state of aggregation; just as we refer also to these molecules, according to similar characters, the property of weight which is observed in sensible masses. Imagine, in fact, an active mass, without losing its homogeneity, to be separated in idea into similar parts of a minuteness imperceptible to our senses, and having for example the figure of spheres or of ellipsoids with two or three axes, or in any intermediate form imaginable. Suppose then that each kind of these particles is assembled and maintained in continuous systems of sensible dimension, by repulsive forces, calorific or others, which should balance their mutual attractions, or by diffusing them in diaphanous fluid media incapable of modifying them by a chemical action, or exercising any peculiar action of deviation upon the polarized light,—I say that all the material systems thus formed would present optical properties similar to those of the active *liquids* under consideration*; that is to say, that each one of them would impress on the planes of polarization of luminous rays deviations in the same direction with all thicknesses in which they may be observed; that the magnitude of these deviations would be proportional to the total mass of the active particles, traversed either in continuity or in succession; and that, lastly, these phænomena would be produced in them without perceptible variation, either in a state of agitation or of repose. This is evident, first, for systems of spherical molecules.

* I specify here, as a condition, the *liquid state*, to avoid the intervention in this statement of the polarizing properties, which the regularity of aggregation developes in solid crystallized bodies,—properties which modify the observable phænomena of deviations produced by molecular action when they coexist with it in one and the same material system, as I shall show hereafter.

With respect to the others, in order that they should produce the same results, there must be attributed to them internal motions, similar to those which everything leads us to admit in real bodies, and to apply to the arbitrarily variable arrangement of their active particles the consequences which follow from the law of large numbers. In fact, when a polarized ray, infinitely thin, traverses a finite thickness of one of these systems, composed of active molecules all similar, they would doubtless be presented to it in all imaginable positions, varying infinitely the length of the course which it would pursue in each of them, as well as the amplitude of the partial deviation which they would individually impress on it. But, on account of their excessive minuteness, joined to their almost infinite multitude in every finite thickness of the system, the relation of the total thicknesses to the total quantities of active matter traversed would only vary by excessively small fractions, as hundred-thousandths, millionths, or still less; which would produce only inequalities of one-hundredth or one-thousandth of a millimetre, or still smaller, in a column of one metre in length. Now, all the rotatory powers hitherto observed being inappreciable to the senses through such small thicknesses, such inequalities will be imperceptible; so that the proportionality of the deviations to the total thicknesses will appear exact. And these deviations will appear also the same, whether the active mass be mechanically agitated, or left in apparent repose. For, on agitating it, we merely cause it to vary the already infinitely diverse positions of the active molecules, which, by the same law of large numbers, cannot sensibly change their mean effect. I must call to mind that I present this idea not as a necessary reality, but as a simple mathematical possibility, which would be logically compatible with all the phænomena observed. Without doubt it may be said that this is only to avoid the difficulty which we have of conceiving the natural and primordial cause of these properties, since we thus only transfer to the constituent molecules of the active masses the same physical actions which these masses present; but all our science consists only of similar reductions which succeed one another indefinitely, without term or limit; and the individual gravity of the molecules of bodies is established on an exactly similar reasoning.

7. Conceiving then a power of deviation thus exercised successively on the plane of polarization of one and the same simple

ray by material molecules independent of one another, I proceed to establish theoretically the observable results which this power should produce through masses of a sensible thickness. I shall afterwards compare these results with facts, both in those cases where the active molecules are individually free, as well as in those where, without being decomposed, they enter into chemical combinations with the active or inactive elements of an ambient medium.

8. I consider, first, a liquid chemically homogeneous, all the constituent molecular groups of which are equally active. I attribute to this system a constant and uniform temperature, which I shall always do, unless I state the contrary. This being agreed on, in the pencil of rays of light supposed homogeneous, which reaches the pupil through the liquid, let us in thought isolate a mathematical, rectilinear ray. This ray will never enter the pupil alone; it will always form part of the luminous cylinder of sensible dimension which the aperture of this organ admits. Such a cylinder may therefore be imagined as composed of a multitude of others of very large lateral dimensions compared to the constituent molecules of the active medium, or at least of the same order, and yet, like them, imperceptible to the senses, without at the same time being wholly null, or even infinitely small in the geometrical acceptation of the word. Each of these luminous threads, in traversing the total mass of active matter which occurs in its course, will experience in its plane of polarization a total deviation α, which, supposing the medium to be of a finite and constant thickness, will be sensibly equal for all the rays of the same nature which enter the eye simultaneously. And for each finite thickness l, this deviation α will depend on the density δ to which the active system is actually brought, since the total mass of active matter which enters into the same volume of one and the same elementary cylinder, varies proportionally to this density. Admitting then that these variations of δ are effected under such conditions that they influence only the intervals of the active groups without modifying their peculiar action on polarized light, which may be ascertained experimentally, as I shall observe presently, all the effects thus produced by one and the same active system with different thicknesses and densities, will be connected one with another by the individuality of the action, which will render them proportional to the total mass of the active groups contained in the finite length l of the

elementary liquid threads of equal diameter, formed under the different densities δ. To connect them then, by a common expression, let $[\alpha]$ be the deviation which the homogeneous liquid under consideration would impress on the plane of polarization of the simple ray chosen as a type, by acting upon it under the same circumstances through the unit of thickness, and with an imaginary density equal also to unit. Then, the density becoming δ, without the energy of the molecular action changing, the deviation through the unit of thickness will be $[\alpha]\,\delta$, in the proportion of the mass of active matter contained in the two fluid columns of sensible dimension and of equal length. Moreover, this length becoming l for the same density, the total deviation will be $[\alpha]\,l\,\delta$. Having then designated by α its magnitude, as it is observed under these new circumstances, we should have*

$$[\alpha]\,l\,\delta = \alpha\,;$$

consequently

$$[\alpha] = \frac{\alpha}{l\,\delta}. \quad \ldots\ldots\ldots \quad (1.)$$

The second member of this equation (1.), which expresses $[\alpha]$, should therefore always present the same numerical value for the different values of δ and of l, when the conditions on which the formula is based are realized; that is to say, when the diversity of deviation assigned to the active groups of the liquid does not change the individual energy of their action on polarized light. The quantity designated here by $[\alpha]$ constitutes what I have called *the rotatory molecular or specific power of bodies.*

9. The only means by which the density of a free liquid can be modified without changing the nature of its *ponderable* elements, is to subject it to momentaneous variations of temperature which contract or dilate it within sufficiently restricted limits for it to return spontaneously to its primitive state, when it is replaced in its original condition. However, these precautions, which determine the identity of the restitution, give no assurance

* I have presented the demonstration of this result several times, and under different forms, in the *Mém. de l'Acad. des Sciences*, particularly t. xiii. p. 116; t. xv. p. 100; t. xvi. pp. 241 and following. But the reasoning upon which I found it here appears to me infinitely preferable, as being independent of all hypothesis, and even of any theoretical notion on the mode of action by which the active molecules influence the luminous principle. This mode of reasoning, established on the distinction of physical and geometrical infinitely small quantities, is the same as Poisson employed to reduce to means the elementary actions which produce magnetic phænomena, capillary effects, and the equilibrium of heat.

that the elementary molecules of the body considered do not undergo temporary changes in their individual constitution during the variations of temperature which the mass undergoes. The numerous experiments made by M. Regnault upon specific heats, with unusual care and precision, render the contrary proposition extremely probable; for by them he has demonstrated that the specific heat of bodies, that is to say the quantity of heat necessary to raise their temperature one degree, has two distinct functions; the effect of the one being to dilate the body, by forcing its constituent particles to separate further from one another; the other, absorbed or dissimulated, so to speak, and uniting with these particles in their new conditions of distance in order to become a physical element of their modified constitution*. This result is entirely conformable to the mechanical conceptions employed by Laplace, and above all by Poisson, to establish the mathematical peculiarities of the equilibrium and movement of heat in material bodies. Now the formula (1.) which we have just obtained for the optical action of homogeneous liquids will, in many cases, render manifest the distinction of these two portions of the total specific heat, and may even, in some cases, lead to an appreciation of their relation. For the values of the density δ being determinable by experiment for the different degrees of temperature to which one and the same active liquid is successively subjected, without any permanent alteration, if the value of $[\alpha]$, calculated with these densities δ, is variable, we may be certain that some portion of the total specific heat has become attached to the constituent particles, and has modified, at least temporarily, their constitution, since it has changed one of their properties. If, on the contrary, the value of $[\alpha]$ is constant, we can only conclude thence this alternative, namely, that the specific heat has been consumed entirely in dilating the liquid under consideration, or that, if a portion is attached to the particles, it has not changed the energy of their action upon polarized light.

10. These tests are much more sure and more sensitive than we should be led to think, considering the little extent of the variations which the densities of liquids experience when they

* *Recherches sur la Chaleur Spécifique des Corps Simples et Composés*, by M. V. Regnault, *Annales de Chimie et de Physique*, tome lxxiii. 2nd series, p. 67; tome i. 3rd series, pp. 189, 200, 207; tome ix. 3rd series, pp. 334, 341 *et passim*.

are not heated to the point of conversion into vapour. They are very easily applicable to diaphanous liquids, except solutions of tartaric acid, because the law of dispersion of the planes of polarization which is nearly common to them, always occasions, in a certain azimuth of the analysing prism, an extraordinary violet-blue (*gris de lin*) tint, which follows the deep blue and precedes the red by an immediate transition, the perception of which furnishes a fixed index of excessive delicacy. In proof of this I shall relate the following experiment, made upon essence of turpentine, although it only presents a simple approximation. I filled a glass tube of a somewhat large calibre, 146¼ millimetres long, and capable of being closed by caps of thin glasses with parallel faces, with a certain sample of this essence. I observed the optical power of the essence through this tube at the temperature of 7°·5 C. The extraordinary violet-blue tint which I took for index became evident in the azimuth $-55°\frac{1}{4}$; that is to say, when the principal section of the analysing prism was removed by this amount from the primitive plane of polarization, toward the left of the observer. I then left the alidade of the prism in this position; and, having closed the tube with its metallic mounting in a tin case of the same calibre, I put the whole into a water-bath, the temperature of which was gradually raised; then, after a certain time, I removed the case and withdrew the tube, which I replaced anew, as quickly as possible, upon the optical apparatus, the alidade of which remained fixed. I cannot exactly state the temperature which the essence had acquired, not having taken the necessary means of measuring it, nor above all to render it fixed; I can, however, form an approximate valuation, because in the first moment when I replaced the tube in observation, it was not too hot to touch it with the naked hands, so that I suppose its temperature may have been about 50° or 60°. The extraordinary tint, which was previously violet-blue, immediately appeared a beautiful red; and to restore to it its first character, I was obliged to bring back the alidade, and consequently the principal section of the analysing prism, 2° toward the primitive plane of polarization. Thus the hot essence caused the planes of polarization to deviate toward the left, less than the cold essence by that quantity through an equal thickness; and this diminution of 2°, visibly manifested by the change of tint, consequently expressed the total change which had been effected in the power of the liquid

column, as well by the rarefaction due to the elevation of temperature, as by the peculiar modification which the constituent molecules had undergone. In proportion as the temperature fell, the new violet-blue image became gradually more and more blue; and the following day, when the liquid had resumed the temperature of 7°·5, I found that, to bring it back to its primitive violet-blue character, it was necessary to move again the azimuth 2° toward the left, that is to say, to bring it back to the same deviation in which it was originally. The change effected in the action of the essence was therefore temporary, and its particles had not undergone any permanent modification in their constitution. I commenced a second time the same experiment, endeavouring to render all the conditions of heating similar; it re-produced exactly the same results*.

Imperfect as this experiment is, as regards the measurement of the temperatures, it may serve as an example of calculation. Let $[\alpha]$ be the molecular power of the essence at the lowest temperature t at which the experiment is commenced, $[\alpha]$ being defined as in § 8. It is observed in the tube of the length l, under its actual density δ, and it has been found to produce there the deviation α upon the type ray, which was in this case the pure yellow ray; for in the general law of dispersion reciprocal to the square of the length of the *fits*, the azimuth of the violet blue or blue-violet image is exactly that of the deviation peculiar to this kind of rays†. Now, according to § 8, the theoretical

* To perform these experiments with the essence conveniently, I first fixed one of the caps of the glass tube by the interposition of a very thin layer of a concentrated solution of gum-arabic, which I applied only near its exterior border, in order that on fixing the tube it might not extend into the interior of the surface which the active liquid should occupy. When this layer was dry it adhered completely. Then, before pouring the essence into the tube by the orifice which had remained open, I applied a similar layer on its margin, and filled it with care, until the column of liquid introduced rose somewhat above it, forming at its free extremity a convex meniscus. I then broke this meniscus by applying the cap, which caused it to adhere; and I completed this adherence by means of a tightening screw terminating the enveloping metallic tube. For these experiments it is well to use a glass tube of a rather large calibre, when a bubble of air may be left in it, which offers a sufficient space for the liquid to expand. If we have specifically in view these experiments, it would be more safe and convenient to adapt a sort of lateral reservoir to the tube for this same purpose. But every one will readily imagine the details which will be most convenient, and I only mention here those which I employed in order to prepare the way for the best arrangements.

† This fundamental proposition has been established theoretically, and afterwards confirmed by experiment, in the memoir, *Sur la Polarisation Circulaire*, inserted in vol. xiii. of the Collection of the Academy.

expression of the deviation, under such circumstances, is $[\alpha]\, l\, \delta$. Since then it was found by observation equal to α, we ought to have

$$\alpha = [\alpha]\, l\, \delta.$$

This is only a reversed application of equation (1.). The essence is now heated and raised to the temperature t', when its density becomes δ'; it is then observed again through the same tube, which I suppose to be of glass, so that we may neglect its longitudinal dilatation, which can be easily taken account of in cases where the experiment is made with sufficient exactness to render it necessary *. If the molecular power of the essence has not changed, the new deviation should be $[\alpha]\, l\, \delta'$. Thus, denoting it by α', we should have

$$\alpha' = [\alpha]\, l\, \delta';$$

this second equation, combined with the preceding one, gives, on eliminating $[\alpha]$, which is common,

$$\frac{\alpha'}{\alpha} = \frac{\delta'}{\delta},$$

or

$$\frac{\alpha' - \alpha}{\alpha} = \frac{\delta' - \delta}{\delta}.$$

The first equation shows that the deviations should be proportional to the corresponding densities; the second denotes that the variations of these two elements should be expressed by the same fraction.

Let us apply this to our experiment. We had at first the primitive deviation α equal to 55° towards the left, then the deviation α' was found 2° less in the same direction. Thus the relation $\frac{\alpha' - \alpha}{\alpha}$ is here $-\frac{2}{55}$ or $-\frac{1}{27{\cdot}5}$; that is to say, the deviation has diminished about $\frac{1}{28}$. Now the elevation $t' - t$ of its tem-

* Let l be the length of the tube at the primitive temperature t, and l' its length at the subsequent temperature t'; l' will be known in function of l by the linear dilatation which the substance of the tube experiences for the difference of temperature $t' - t$; then, in order to reduce the two observations to one and the same thickness, the primitive deviation α should be increased by a quantity proportional to $l' - l$, which would change it into $\alpha\left(1 + \frac{l' - l}{l}\right)$, after which it might be employed concurrently with the deviation α', as if they had been both observed in the same tube l' of constant length under the respective densities δ and δ'.

perature must have been not far from 50°; and, as the density of the essence of turpentine decreases about $\frac{1}{14}$ in passing from 0 to 100°, its diminution, for half of this interval, is also nearly $\frac{1}{28}$; that is to say, equal to the decrease of the rotatory power. Thus, judging from these numbers, the whole specific heat of the essence would be employed in changing its volume, without its molecular constitution experiencing any alteration. But it may be imagined that such results ought to be established by precise measurements, placing the tubes of observation in metallic coverings, which would allow them to be kept at constant and known temperatures. I have long since constructed an apparatus of this kind, but have not had leisure to make use of it, and I fear that I shall not find an opportunity.

11. The aqueous solutions of tartaric acid present an opposite effect to that just mentioned. The deviations α of one and the same ray are seen in them *increasing* for one and the same thickness, in proportion as the temperature rises, notwithstanding the diminution in density which should weaken them. This may be instantly proved by heating for some minutes, with a spirit-lamp, the tube which contains them, whilst it is placed upon the optical apparatus. The increase of the deviations is immediately manifested; it then stops after the lamp is withdrawn; and they finally return slowly to their primitive amplitude, in proportion as the previous temperature is re-established. The specific heat introduced into these solutions is therefore far from being wholly consumed in their changes of volume. The molecular constitution of the acid which they contain is momentaneously modified by it, since it is that which communicates to water the rotatory power, by forming with it a true combination, as I shall prove hereafter. We see, by these two examples, how much this class of observations, which allows us, so to speak, to witness the calorific modifications of material particles, may give us new ideas on the part which should be attributed to the imponderable principle of heat in the constitution of bodies,—a question which has hitherto remained inaccessible to other physical experiments. But, in order to be able to place reliance upon the indications which the optical characters may furnish on these invisible phænomena, we must extend their theory to

other more sensible applications, and this I shall do in what follows.

12. The permanence, at least very approximate, of constitution which we have just seen in the molecules of the essence of turpentine when their mutual distances are increased by a moderate elevation of temperature, leads us to conceive how they still preserve an optical power of the same nature and of the same direction when separated from one another so far as to reduce them to the state of elastic vapour in motion. The only experiment of this kind which has been attempted, and which was unfortunately incomplete, was made by transmitting the vapour of the essence in a continuous current through a metallic tube 15 metres long, inclosed in another tube in which it first circulated, in order to maintain in it an external temperature sufficiently elevated. After all the air was expelled, the column of vapour in motion was observed to impress on the polarized light a very perceptible deviation in the same direction as that of the liquid, that is to say directed also towards the left, and producing in the same manner coloured images of variable tints, which succeeded one another in a similar order, when the principal section of the analysing prism was progressively brought into different azimuths around the primitive plane of polarization. Two observers, who assisted me in this experiment, were witnesses of these facts. Unfortunately an explosion which occurred in the apparatus prevented my profiting by the arrangements which I had prepared to measure the temperature of the current and its elastic force when it should have arrived at a fixed state, which would have enabled me to calculate the density of the vapour and to compare the relative energy of the molecular conditions in two such different states of the same body. If this experiment were repeated and extended to various active essential oils, it would doubtless furnish extremely interesting results, especially on comparing those which would be obtained as well on such of these bodies as might undergo a certain degree of vaporization without decomposition, as also for such as this operation, repeated or continued for some length of time, would progressively alter.

13. The individuality of power, however, which the active groups preserve in this state of indefinite separation, induced by vaporization, indicates a much more simple and convenient means of varying their intervals without altering their influence

upon light; this is to diffuse them by dilution in an inactive liquid which does not modify them chemically; and this will also offer the advantage of evidencing the same kind of action in a great number of substances usually solid and opake, which cannot be liquefied by heat without the risk of altering them, or which, if they are transparent in a solid state, are at the same time crystallized, which developes in them phænomena of polarization peculiar to this kind of aggregation, by which the effects of their molecular power are modified, or even completely dissimilated.

14. For greater simplicity, let us at first admit that the solvent employed does not enter into actual combination with the constituent groups of the active substance, and that it offers to them only a space in which they can distribute themselves uniformly. Let E be the weight of the inactive liquid employed, P the weight of the active substance mixed in it, which may be indifferently liquid or solid; and for shortness let us make

$$\varepsilon = \frac{P}{P + E};$$

ε will represent the ponderable proportion of the active substance contained in each unit of weight *of the mixture*. Let us designate, as before, by $[\alpha]$ the deviation which this substance would produce on a simple ray selected as type, if it could be observed isolated, *in the state of disaggregation*, through the unit of thickness, and under a density equal to 1. Then, the density of the mixture being δ, and the observation being made through a tube of a length l, the total deviation which it would produce on the type ray, under these circumstances, if it were entirely formed of the active substance, would be $[\alpha] l \delta$, as before. But the deviation α really produced will be less than this, in the proportion of ε to 1; that is to say, proportionally to the relative mass of the active groups actually contained in the total mass of the length l, under the density δ. Thus it will be only $[\alpha] l \varepsilon \delta$. Then designating it by α, we shall have, by eliminating $[\alpha]$ from the equation,

$$[\alpha] = \frac{\alpha}{l \varepsilon \delta}, \quad \text{or } [\alpha] = \frac{\alpha (P + E)}{P l \delta}. \quad . \quad . \quad . \quad (2.)$$

The second member of this new equation is composed wholly of observable quantities. On calculating it according to experiment, for different values of its elements l, ε, δ, and α, it ought

always to present a constant value, when the physical conditions taken as basis of the reasoning have been realized; that is to say, when the active groups shall only have diffused themselves in the inactive medium without being chemically modified by it, and also without modifying the primitive inactivity which the latter is supposed to have for light; or again, if the combination which may be presumed to take place between the two substances is sufficiently feeble that these modifications may be inappreciable, which would greatly extend its applicability. When the active substance is observed isolated, E becomes null, which renders ε equal to 1, and the expression of $[\alpha]$ is reduced to the preceding (1.) of § 8, as should be the case from the identity of circumstances to which the experiment is reduced. This expression of $[\alpha]$, given by the equation (2.), thus reproduces more generally *the molecular or specific rotatory power of bodies* than the equation (1.), which supposed the active substance observed isolated in the liquid state.

15. I will relate, as an example, a very simple application which confirms the justness of association of all its elements. Take two cylindrical tubes, A, B, the lengths of which are l_1 and l_2, the latter larger than the former: A is filled with an active liquid, and the same length l_1 is poured into the tube B, which is then filled with an inactive liquid, whose chemical action on the other is null or insensible. We then observe A, which produces the deviation α_1 on the type ray; then B, which produces the deviation α_2 on this same ray. The experiment always gives $\alpha_2 = \alpha_1$. This follows from the formula (2.).

To prove this, let us take δ_1, the proper density of the active liquid in the circumstances in which it is employed. Since it produces the deviation α_1 through the thickness l_1, when it is observed alone, by designating by $[\alpha]_1$, its proper molecular power, we shall have, by the formula (1.) or by the formula (2.) applied to these circumstances,

$$[\alpha]_1 = \frac{\alpha_1}{l_1 \delta_1}.$$

Let P_1 be the absolute weight of this same active liquid occupying the length l_1 in the tube B, and V_1 its volume. We shall evidently have

$$P_1 = V_1 \delta_1;$$

to this weight P_1 a certain weight P_2 of an inactive liquid is added, which fills the tube B. Let V_2 be the total volume of

the mixture thus reduced to the total length l_2; and let δ_2 be likewise its density, which may be established with or without modification of the partial volumes. We shall again have

$$P_1 + P_2 = V_2 \delta_2.$$

These are the circumstances assigned to the experiment. To calculate the theoretical result, we must seek the ponderable proportion ε_2 of the active substance in the mixed system. Its expression is evidently

$$\varepsilon_2 = \frac{P_1}{P_1 + P_2} = \frac{V_1 \delta_1}{V_2 \delta_2}.$$

Now, the molecular power of this substance being $[\alpha]_1$, its presence in the proportion ε_2, in the system whose density is δ_2, will produce, through the thickness l_2, the deviation $[\alpha]_1 \varepsilon_2 l_2 \delta_2$; so that, if we call this resulting deviation α_2, we ought to have

$$\alpha_2 = [\alpha]_1 \varepsilon_2 l_2 \delta_2.$$

Replacing $[\alpha]_1$ and ε_2 by their above-formed expressions, the densities δ_1 and δ_2 disappear, and there remains

$$\alpha = \alpha_1 \frac{V_1 l_2}{V_2 l_1}.$$

But as the volumes V_1, V_2 are both measured in the same cylindrical tube B, in which they occupy respectively the lengths l_1 and l_2, they are proportional to those lengths, which gives

$$\frac{V_1 l_2}{V_2 l_1} = 1;$$

consequently

$$\alpha_2 = \alpha_1,$$

which is precisely the result observed.

I long ago performed this experiment, by mixing essence of turpentine with olive oil bleached by a long exposure to the sun. It may be very easily repeated on aqueous solutions of cane-sugar, starch-sugar, or dextrine, diluted with water at a constant temperature. Nevertheless, when the observation is carefully made, a very small inequality is perceived, or rather suspected, between α_1 and α_2, when the primitive solution is very concentrated; this arises from a feeble reaction which then takes place between the active substance and the water present, as we shall hereafter prove in other examples, in which such a reaction is indubitable.

16. The following is another more complex application of the formula (2.), which is curious and important from the results which it furnishes.

Take two active liquids which can mingle with one another without appreciable chemical reaction, at least for a short space of time; for example, essential oil of turpentine and essential oil of lemon. Let δ_1, δ_2 be their densities at the ordinary and constant temperature at which the experiment is performed. The deviations which these liquids produce on the type ray in tubes of known lengths are successively observed, and these results reduced to the same thickness L by the law of proportionality. Let α_1, α_2 be the corresponding deviations thus deduced. If we call $[\alpha]_1$, $[\alpha]_2$ the rotatory powers peculiar to the two liquids, we shall have by these observations

$$[\alpha]_1 = \frac{\alpha_1}{L\,\delta_1}, \qquad [\alpha]_2 = \frac{\alpha_2}{L\,\delta_2}.$$

Now let us take a weight P_1 of the first liquid, a weight P_2 of the second, then mix them, and the result is a mixed liquid whose density is δ. What will be the deviation α produced on the type ray by this system, when observed through a tube of the length l?

I first find the ponderable proportions ε_1, ε_2 of the two liquids in the mixture formed under these conditions. They will evidently be

$$\varepsilon_1 = \frac{P_1}{P_1 + P_2}, \qquad \varepsilon_2 = \frac{P_2}{P_1 + P_2};$$

then, this mixture having the density δ, when observed through the length l, each of the two liquids will there produce individually the partial deviation peculiar to its nature and to its ponderable proportion. This will give, for the first, $[\alpha]_1\,\varepsilon_1\,l\,\delta$; for the second, $[\alpha]_2\,\varepsilon_2\,l\,\delta$. The sum of these two quantities then will compose the total deviation which should be observed under these circumstances; and since we designate it by α, we should have

$$[\alpha]_1\,\varepsilon_1\,l\,\delta + [\alpha]_2\,\varepsilon_2\,l\,\delta = \alpha.$$

Putting for $[\alpha]_1$, ε_1, $[\alpha]_2$, ε_2, their expressions previously formed, and transferring the common factors into the second member, this equation becomes

$$\alpha_1 \frac{P_1}{\delta_1} + \alpha_2 \frac{P_2}{\delta_2} = \alpha \frac{(P_1 + P_2)\,L}{l\,\delta}.$$

As a special application, let us propose to form the mixture in such proportions that the resulting deviation α may be exactly null for the type ray. The condition of this result will evidently be

$$\alpha_1 \frac{P_1}{\delta_1} + \alpha_2 \frac{P_2}{\delta_2} = 0.$$

The relations $\frac{P_1}{\delta_1}, \frac{P_2}{\delta_2}$ being essentially positive, the requisite compensation can only take place when the deviations α_1, α_2 have opposite signs, that is to say when the two mixed liquids turn the plane of polarization of the type ray in different directions. The essential oils of turpentine and of lemon are in this case: the first turns the planes of all the rays towards the left, the second towards the right of the observer.

With respect to the proportions of the mixture, let V_1 be the volume of the first liquid occupied by the weight P_1, at the temperature at which the experiment is performed, and V_2 the analogous volume occupied by the weight P_2, we shall evidently have

$$P_1 = V_1 \delta_1; \; P_2 = V_2 \delta_2.$$

These expressions of the weights P_1, P_2 being substituted in our equation of condition, the densities disappear, and there remains

$$\alpha_1 V_1 + \alpha_2 V_2 = 0;$$

that is to say, the two liquids must be mixed in volumes reciprocally proportional to the deviations which they produce, in tubes of equal length, on the type ray for which their actions are to be compensated.

17. I have published the details of a similar experiment on the essential oils of lemon and of turpentine, in the *Comptes Rendus de l'Académie des Sciences*, t. ii. p. 540 *et seq.* I shall only relate here the general results. The compensation was established for the red ray, transmitted through a glass coloured by the protoxide of copper. The compensation was very exact *for it* when the mixture had been effected in the relations of volume indicated by the formula. But it was not quite exact for the other rays of the spectrum; for, on placing the principal section of the analysing prism in the primitive plane of polarization of the incident pencil, the extraordinary image, which should have been null if the compensation of the deviations had been general, was feebly but sensibly apparent; so that on moving the prism a little to the right or the left of that primitive azimuth, feeble signs of coloration were distinctly observed in the extraordinary image, which soon disappeared when the azimuth continued to increase in the one or other direction. This experiment proves, therefore, that the dispersion of the planes of polarization is not effected rigorously, but only very nearly, according to the same law in the two oils, and doubtless also in other substances possessing rotatory powers. Thus the

reciprocal proportion of the dispersion to the squares of the lengths of the *fits* is only an approximation of very general application, and not a property of the luminous principle, as had previously been supposed. This has been since completely proved by the observations made on the aqueous solutions of tartaric acid, since the dispersion of the planes of polarization is effected by it according to wholly different laws. But before these last phænomena were known, the dispersions observed in all other colourless active liquids produced successions of tints so approximately similar, when the analysing prism accomplished its revolution, that we might have thought them identical, and that we may still, without inconvenience, employ them as such in a multitude of observations. The exact restitution of the type ray to its primitive plane of polarization in the mixed system composed according to the theoretical proportion of volumes, and the approximative return to the same plane, which is effected in all the other rays, demonstrate the molecular character of this kind of action by the most rigorous proof which can be conceived, since these restitutions are only effected by the final equivalence of an almost infinite multitude of deviations in contrary directions, experienced successively by the luminous elements during the whole length of their passage*.

* I have repeated this experiment on two liquids whose mode of dispersion might have been presumed, and was found in fact much more similar. The first, which I shall designate by S, was syrup of pure cane-sugar diluted with water; the second, which I shall call S′, was another syrup of the same sugar, which M. Soubeiran had treated with hydrochloric acid, and then saturated with a great excess of very pure marble; so that it consisted of a solution of uncrystallizable sugar mixed with chloride of calcium. These two liquids were observed with the naked eye, in glass tubes of nearly equal length, taking for type of the deviations the extraordinary bluish violet tint. For S′ the length was $146^{m}{\cdot}25$, and the deviation $-25^{c}{\cdot}33$, directed toward the left of the observer. For S the length was $147^{m}{\cdot}75$, and the deviation $+53^{c}$, directed toward the right; this reduced to $146^{m}{\cdot}25$ by the law of proportionality, becomes $+52^{c}{\cdot}46$. I then mixed S′ with S in the relations of volume inverse to those numbers, or as 207 to 100, and I observed the mixture through a tube 501^{mm} long, which more than tripled the effects of all the errors which I might have committed. The compensation was total. The extraordinary image was null in the azimuth of primitive polarization, and presented no sensible trace of coloration beyond that azimuth, just as if a completely inactive liquid had been interposed in the course of the ray. But I presume that the compensation is destroyed in time, either by the spontaneous fermentation of the liquid S, or by the action which the chloride may exercise upon it, which would cause a resultant toward the left. On this account I kept the mixture in a large glass simply covered by a capsule, in communication with the air, and I shall mention in the latter part of this memoir the effects which it will have undergone.

18. But the physical conditions which we have hitherto assigned to the experiment are still very limited. When an active substance, solid or fluid, is dissolved in an inactive liquid, or mixed with it, so that a continuous liquid results, in which the chemical groups peculiar to each of the two bodies preserve their primitive constitution without mutual decomposition, it is doubtless by a rare exception that these groups may be supposed to insinuate themselves amongst one another, and to diffuse themselves with uniformity throughout the whole space, remaining wholly insensible to their mutual presence. We ought rather to suppose that in general these primitive groups, or some of them, enter into actual combination, so as to compose momentaneously new groups, which may act upon polarized light quite otherwise than those from which they are derived; and this conception evidently includes, as a particular case, that of simple mixture, which we considered above. To prepare formulæ applicable to the experiments generally, it is necessary to adapt them to that possible diversity of conditions. In order to simplify the question, I will suppose that all the systems under consideration are formed at a constant temperature, and that they are composed solely of the same active substance, successively associated with different and progressively increasing doses of one and the same inactive liquid, under the sole condition that the mixed system can subsist in a state of fluidity. In these circumstances, limited as they are, chemists are of opinion that every medium thus formed may simultaneously contain several combinations of the two bodies, constituted in the different proportions of simple multiples. Although such a diversity appears rather capable of being occasioned by the progressive effect of time and variable circumstances, than from a common and instantaneous reaction, I shall not exclude it. But I shall suppose that the constitution of each mixed system, whatever it be, remains constant whilst its optical effect is observed. This will be conformable to experiment for the systems which we shall consider, since their action upon polarized light is always found to be the same, when they are replaced in the same conditions of quantities and of temperature.

19. Taking then any one of these systems with its actual constitution, however complex it may be supposed, it may happen that the quantity of the inactive liquid employed may be more than sufficient, or sufficient, or insufficient, to saturate com-

pletely the active substance which it contains in the state of combination, single or multiple, to which it has spontaneously arrived. In these three supposable cases, when the first or the second is realized, the new chemical groups formed by the active substance will be complete, and an ulterior addition of the inactive liquid will not change them. In the last case, on the contrary, it will change them. These two phases of stability and of instability will cause distinct optical effects, which I shall proceed to characterize successively by corresponding formulæ.

20. In the first, that of supersaturation or of exact saturation, I suppose first that the active substance forms with the inactive liquid *one sole* kind of combination, in which each of its particles is united with a certain fixed proportion of this liquid. The rest therefore of this liquid which shall not have been absorbed will offer a free space in which the combined groups may diffuse themselves uniformly with the permanent constitution they have acquired. To express this result, let P be the total weight of the active substance employed, and n P the weight of the inactive liquid necessary to saturate P in the uniform mode of combination which we suppose to be effected. The multiple n, whether it be entire or fractional, will have a constant value in the case of fixity of composition of the groups which we suppose. Designating then by E the total weight of the inactive liquid employed, every similar system will contain the weight P + n P, or $(n + 1)$ P, of combined groups, and the weight E − n P of free inactive liquid; this last quantity being necessarily always positive or null, but never negative for the systems here considered. This being assumed, I make, for abbreviation,

$$\varepsilon = \frac{P}{P + E}; \qquad \varepsilon_1 = \frac{(n + 1) P}{P + E},$$

whence results

$$\varepsilon_1 = (n + 1)\,\varepsilon.$$

ε will represent, as before, the proportion by weight of the active substance contained in each unit of weight of the system, and ε_1 the proportion by weight of the new combined groups in it. Let δ be the actual density of this system, l the length of the tube through which it is observed, α the deviation which it then produces on the type ray. Since the new combined groups may exert on polarized light an action generally different from

that which the primitive groups of the active substance would exert isolated, I designate by $[\alpha]_1$ the deviation which would be produced on the type ray, through the unit of thickness, by a diaphanous system composed solely of these new groups, and having an imaginary density 1 at the temperature at which the experiment is made. Returning then to the proposed system, since these groups are there uniformly diffused in an inactive liquid, which is supposed to have no modifying action upon them, the reasoning in § 14 is applicable to them, that is to say, that the observed deviation α should be equal to the product $[\alpha]_1 \varepsilon_1 l \delta$ under such circumstances. Establishing then this equation, substituting for ε_1 its value in ε, and deducing $[\alpha]_1$, we obtain

$$[\alpha]_1 = \frac{\alpha}{(n+1)\, l\, \varepsilon\, \delta}; \quad \ldots \quad (3.)$$

or

$$(n+1)\,[\alpha]_1 = \frac{\alpha\,(\mathrm{P}+\mathrm{E})}{\mathrm{P}\, l\, \delta}. \quad \ldots \quad (3.)$$

The function $(n+1)\,[\alpha]_1$ is therefore in this case absolutely of the same form as the function $[\alpha]$ of § 14; and, like it, it is composed entirely of observable quantities. Now, since the new-formed groups are supposed not to be modified by the indefinite addition of the superabundant portions of E, $[\alpha]_1$ ought to be constant by the identity of these active groups in all the similar systems in which E is in excess; and the multiple n ought likewise to be constant, by the fixity of their composition, in these same systems. Therefore, if the numerical value of the function $\frac{\alpha\,(\mathrm{P}+\mathrm{E})}{\mathrm{P}\, l\, \delta}$ be calculated according to the observable elements composing it, we ought always to find it the same in all the systems thus derived from one another by progressive additions of E, when the physical conditions supposed in the reasoning have been realized; that is to say, when the quantity of inactive liquid employed shall surpass or equal the quantity necessary to saturate the active substance present, in the sole kind of fixed combination which it is supposed to form with it. I include in this statement the case of equality which corresponds to exact saturation, because it is contained in the same formula. In fact, if the weight E of the inactive liquid is just sufficient to saturate P in the combination formed, E becomes equal to n P. Substituting this value of E in the equa-

tion (3.), the multiple $n + 1$ disappears, and there remains for this particuliar case

$$[\alpha]_1 = \frac{\alpha}{l\delta}.$$

The expression of $[\alpha]_1$ coincides then with that of $[\alpha]$ given by the equation (1.) of § 8, for active liquids chemically homogeneous. This should be the case, since the mixed system being then composed solely of new-formed groups, which are all identical, it becomes chemically homogeneous, as is supposed in equation (1.).

If, no longer limiting E, the primitive groups of the active substance are supposed not to combine with any, or only with an insensible proportion of the inactive liquid, n becomes null, or may be neglected; and the expression (3.) of $[\alpha]_1$ is reduced to

$$[\alpha]_1 = \frac{\alpha}{l\varepsilon\delta}; \qquad \text{or } [\alpha]_1 = \frac{\alpha(P + E)}{Pl\delta};$$

it is then found to be identical with that of $[\alpha]$ given by the equation (2.) of § 14, for the case in which the active substance is diffused in the inactive liquid by simple mixture, which accords in fact with the identity of the circumstances thus introduced into the equation (3.).

21. I now consider the general case in which the total weight P of the active substance is divided spontaneously into any number of partial weights $P_1, P_2, P_3, \ldots P_i$, which would form as many fixed, but different, combinations with proportions in weight of the inactive liquid designated by $n_1 P_1, n_2 P_2, \ldots n_i P_i$; admitting always that the total weight E of this liquid surpasses or equals the sum $n_1 P_1 + n_2 P_2 + \ldots + n_i P_i$, in order that there may be supersaturation, or exact saturation, in all the systems thus composed. The condition of partition of P will require first that we have

$$P = P_1 + P_2 + P_3 \ldots + P_i;$$

then the absolute weights of the partial combinations will be respectively

$$(n_1 + 1) P_1, (n_2 + 1) P_2, \ldots (n_i + 1) P_i;$$

and designating their ponderable proportions in the mixed system, by the letter ε successively affected by the same signs, we have

$$\varepsilon_1 = \frac{(n_1 + 1) P_1}{P + E}, \varepsilon_2 = \frac{(n_2 + 1) P_2}{P + E}, \ldots, \varepsilon_i = \frac{(n_i + 1) P_i}{P + E}.$$

Let δ be the actual density of the system, l the length of the tube through which the observation is made; and let us call

$$[\alpha]_1, [\alpha]_2, \ldots, [\alpha]_i$$

the deviations which would be produced on the type ray through the unit of thickness, by as many diaphanous systems composed solely of a same kind of these complex groups, under a same imaginary density equal to 1, at the temperature at which the experiment is made. Returning then to the proposed system, since all these groups are there uniformly diffused in an excess of the liquid supposed to have no longer any modifying action on them, the observed deviation α should be equal to the sum of all the partial deviations which they might individually produce, in the ratio of their proportions by weight in the mixed system, that is to say, we shall have

$$[\alpha]_1 \varepsilon_1 l\delta + [\alpha]_2 \varepsilon_2 l\delta \ldots + [\alpha]_i \varepsilon_i l\delta = \alpha;$$

on substituting in this equation for $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_i$ their above-formed expressions, we shall readily have

$$(n_1+1)[\alpha]_1\frac{P_1}{P}+(n_2+1)[\alpha]_2\frac{P_2}{P}+\ldots(n_i+1)[\alpha]_i\frac{P_i}{P}=\frac{\alpha(P+E)}{Pl\delta}. \quad (4.)$$

The relations $\frac{P_1}{P}, \frac{P_2}{P}, \frac{P_3}{P}$ are individually constant in all the systems of the same nature which are supersaturated, or only saturated with the inactive liquid, since the weight P of the active substance will always be distributed between all the combinations in the same relations, in virtue of the stability attributed to them. The powers $[\alpha]_1, [\alpha]_2, \ldots [\alpha]_i$ will also be constant, from the individual identity of their composition; and the multiples $n_1, n_2, \ldots, n_i$ will be equally so, since they express the fixed proportions of the inactive liquids which enter into each of the groups. The first member of the equation (4.) will thus be constant in all similar systems in which E is in excess, and the same holds good with the second member, which is equal to it. Therefore, if the numerical value of the function $\frac{\alpha(P+E)}{Pl\delta}$ be calculated according to the observable elements which compose it, we should find it the same in all the systems of like nature in fixed combinations, which will be derived one from another by successive additions of the inactive liquid, when the quantity of this liquid employed shall surpass or equal that necessary to complete these combinations. The optical

character which will distinguish this complex but fixed state will therefore be the same as for systems in single combination, or for simple mixtures, since it will be expressed by the constancy of the same function, whose absolute values can alone differ in these various systems and states. In consequence I shall call it, for the sake of shortness, the *characteristic function* of each system.

22. I now consider the second phænomenal phase indicated in § 19,—that in which the weight employed E of the inactive liquid is insufficient to saturate the weight P of the active substance present. Then, in the fluid system supposed to result from their association, P forms with E chemical groups, homogeneous or heterogeneous, which are, at least in part, incomplete; so that any ulterior addition of the liquid E changes the molecular state of the system. Among all the modes of internal constitution which may, abstractedly, result under this influence of unsatisfied affinities, I shall distinguish three which the habitual experience of chemical reactions renders the most supposable, and I proceed to assign the optical characters which their progressive variations should present.

23. We may conceive first that the liquid E is divided equally among all the constituent molecules of the active substance, so as to form with them as many identical and not saturated chemical groups. Then the mixed system P + E being chemically homogeneous in all the states of non-saturation to which it may be progressively brought, the reasoning employed in § 8 becomes applicable to it for each of these successive proportions. If therefore with the density δ it produces the total deviation α on the plane of polarization of the type ray, when observed through the thickness l, the proper power $[\alpha]_1$ of the chemical groups composing it will be expressed by the formula

$$[\alpha]_1 = \frac{\alpha}{l\delta}.$$

Then, in proportion as the relative doses of the liquid E shall vary, still remaining below the point of saturation of P, the individual constitution of the mixed groups will vary; and without doubt their peculiar power $[\alpha]_1$ will likewise vary in consequence, since it could remain constant among such changes only by a special exception. But its variability, manifested by that of the relation $\frac{\alpha}{l\delta}$, will be the only circumstance that can be

proved, since the values of this relation are not connected by any law of succession which could be theoretically foreseen.

24. I put now a second case, the inverse of the preceding, where the liquid E is not divided equally among all the constituent molecules of P, but is specially absorbed by some which form with it a complete and saturated combination, subject to a certain fixed proportion, which I designate by the integer or fractional multiple n. Then, the portion of P which does not enter into this combination, is diffused in the system, preserving its primitive optical properties. I do not suppose that it dissolves in it, uniting by chemical combination with the perfect groups already formed, because in this manner the case of the preceding paragraph would be reproduced with the same indetermination.

Let P_1, P_2 be the two portions into which P is separated. P_1 combining with E to saturation in the relation n, and P_2 remaining free, the conditions of the phænomenon will be

$$P = P_1 + P_2, \qquad E = n P_1.$$

Let us designate as before by $[\alpha]_1$ the rotatory power peculiar to the newly-formed groups, and by $[\alpha]$ the analogous power of the active substance observed in the isolated state. Let us call δ the density of the mixed system, l the length of the tube through which it is observed, and α the total deviation which it produces on the type ray under these circumstances. It will be easy, by the foregoing principles, to form the theoretical expression of α. For, first, the total weight of the combined groups being $P_1 + n P_1$, their proportion in weight in the mixed system will be $\frac{P_1 + n P_1}{P + E}$; so that having the proper power $[\alpha]_1$, the whole will produce the partial deviation $[\alpha]_1 l \delta \frac{(P_1 + n P_1)}{P + E}$. Then the weight of the active substance remaining free being P_2, its proportion by weight in the system will be $\frac{P_2}{P + E}$, which will produce the partial deviation $[\alpha] l \delta \frac{P_2}{P + E}$. Since then the sum of these two deviations should compose the total deviation α observed, the condition of this equality will give, on transposing to the second member the common factors,

$$[\alpha]_1 (P_1 + n P_1) + [\alpha] P_2 = \frac{\alpha (P + E)}{l \delta}.$$

The quantities P_1, P_2, into which the total weight P is decom-

posed, are not known separately, but their analytical expression is deduced from the two equations to which we have subjected them generally. For we have

$$P_1 = \frac{E}{n}, \quad P_2 = P - \frac{E}{n}.$$

Eliminating P_1 and P_2 by these expressions, our resulting equation takes the following form:—

$$[\alpha] + \frac{\{(n+1)[\alpha]_1 - [\alpha]\}}{n} \frac{E}{P} = \frac{\alpha(P+E)}{P l \delta}. \quad (5.)$$

Supposing, as we do, that the experiment is always performed at the same temperature, $[\alpha]$ will be constant from the identity of condition which the active substance to which it belongs maintains. $[\alpha]_1$ will also be constant, from the identity of composition of the new groups, completely saturated, which the portion P_1 of E is supposed to form with the inactive liquid. Lastly, the multiple n will be likewise constant, since the proportion in which the combination takes place is that of complete saturation. Consequently, when the division of the active substance shall take place as we suppose, if the experiment be repeated for different values of P and of E at the constant temperature adopted, the numerical value of the function $\frac{\alpha(P+E)}{P l \delta}$ should be variable, as the ordinate of a right line of which $\frac{E}{P}$ is the abscissa; and this experiment, which is easily made, will show with certainty whether the supposed division of the active substance takes place or not in the systems under consideration. The application of this form is limited by the conditions of the supposition itself, that is to say, when the weight E of the inactive liquid suffices to saturate P entirely. Then the free portion of P, which we have designated by P_2, becomes null, which gives

$$P = \frac{E}{n};$$

consequently

$$E = n P.$$

On substituting this particular value of E in our general equation, $[\alpha]$ disappears, as well as the multiple n, and there remains

$$[\alpha]_1 = \frac{\alpha}{l \delta};$$

We then fall back on the equation which we have already found in § 20, for the case of complete saturation of the whole active mass P, as ought evidently to be the case, since we thus return to the same circumstances.

25. We might, lastly, conceive another variable mode of non-saturated constitution, which would enter into that which we have considered in § 21, except that it would not remain fixed. This would consist in supposing that for each weight E of inactive liquid associated with the same weight P of the active substance, P forms a certain number of combinations of different orders, saturated or supersaturated, which remain stable both with respect to their composition and their number, until the portion of E, which is in excess relatively to them, attains a certain value; after which a new division of P would take place, giving rise to other saturated combinations, and consequently to a new state of the system, which would in like manner be maintained up to a certain limit of E relatively to P, after which it would change anew. On applying the reasoning in § 21 to each of the temporarily fixed systems which would compose such a succession, we find that the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$ varies by abrupt intervals, between each of which its value will remain constant; and this mode of variation, if observed, would show the existence of the successively changing mode of constitution, to which it corresponds.

26. I have consulted very experienced chemists on the different forms of combinations which may be considered supposable, under the circumstances which we have admitted, that is to say when an active substance is placed in presence of an inactive liquid, at a constant temperature, without mutual decomposition, and for all relative proportions of the two bodies compatible with the state of fluidity. They have not indicated others than those which I have just specified, attributing to them very different probabilities of realization. For this reason I shall collect here the different propositions bearing on the subject, as well as the optical characters derived from them, so that their connection may become more apparent, and that it may suffice to recall them when required.

27. When a constant weight P of an active substance is dissolved at a constant temperature in a variable weight E of an inactive liquid, with which it may enter into a more or less inti-

mate combination without mutual decomposition, the realization of this fact presents two distinct phases.

1. The weight E is more than sufficient to saturate P, and to bring it to a fixed state, which a further addition of the liquid E does not alter.

2. The weight E is insufficient for this saturation, and a further addition of the liquid E changes the combinations which P has formed. The case of an exact saturation is common to these two phases, and forms the transition from the one to the other. Each of them may, moreover, be realized in imagination by several distinct modes, which present different optical characters, and which I shall successively enumerate.

FIRST PHASE.—*The weight* E *of the inactive liquid is more than sufficient, or just sufficient, to saturate* P.

First Case.—The active substance P takes in combination none, or only an insensible portion of the inactive liquid E.

Then, in virtue of § 14, the characteristic function

$$\frac{\alpha\,(P + E)}{P\,l\,\delta}$$

is constant, whatever be the weight of E, and even whatever be the nature of the inactive liquid which composes E, provided the condition expressed in the statement be satisfied. The mixed system is a simple mixture of P and of E.

Second Case.—The weight P of the active substance forms with the inactive liquid one or more fixed combinations, into which this liquid enters in any proportions, $n_1 P_1$, $n_2 P_2$, ..., $n_i P_i$, the surplus of E remaining free.

Then, in virtue of §§ 18, 19, 20 and 21, the characteristic function

$$\frac{\alpha\,(P + E)}{P\,l\,\delta}$$

is again constant for a same inactive liquid, whatever be the weight of E. But its absolute value may, and even must generally be different for inactive liquids of different nature, associated with the same active substance, for it could only be equal by exception. When this diversity of constant values manifests itself in changing the inactive liquid, it will show with certainty that the state of combination, simple or multiple, takes place in some of the mixed systems.

SECOND PHASE.—*The weight* E *of the inactive liquid is insufficient, or but just sufficient, to saturate* P.

The general character of this second phase consists in the function $\frac{\alpha(P+E)}{Pl\delta}$ never being constant when the relation $\frac{E}{P}$ varies.

First Case.—The weight E of the inactive liquid is divided equally among all the constituent molecules of the active substance, so as to form so many chemical groups identical among themselves and imperfectly saturated. For each given value of the relation $\frac{E}{P}$, the mixed system is chemically homogeneous, but the constitution of the groups which compose it changes continually with this relation.

Then, by virtue of § 23, the function

$$\frac{\alpha}{l\delta}$$

varies continually for a same inactive liquid, in proportion as the relation $\frac{E}{P}$ changes, and it ought likewise to vary for the same value of this relation when the inactive liquid is different. At least it could only preserve the same value in such circumstances, by a particular exception, as it expresses the rotatory power of the new chemical groups occasionally formed. For that reason the law of its variability cannot be foreseen. If this mode of variation subsists for all the values of the relation $\frac{E}{P}$ relative to a same inactive liquid, without the function $\frac{\alpha(P+E)}{Pl\delta}$ ever becoming constant, this would prove that the active substance cannot be completely saturated by the inactive liquid, whatever amount of it be employed.

Second Case.—The total weight P of the active substance separates spontaneously into two portions, one of which combines with E to saturation, and the other remains free.

Then, in virtue of § 24, the characteristic function

$$\frac{\alpha(P+E)}{Pl\delta}$$

being calculated successively for different values of the relation $\frac{E}{P}$, relative to one and the same inactive liquid, will be variable as the ordinate of a right line, of which $\frac{E}{P}$ would be the

abscissa. The inclination of this right line on the axis of $\frac{E}{P}$ ought generally to be different, when the nature of the inactive liquid changes, or at least it will only be constant by exception. But the value of the initial ordinate corresponding to $E = 0$, will be constant in all these right lines, since it ought always to reproduce the proper power $[\alpha]$ of the active substance considered isolated. These rectilinear forms will likewise apply when the weight E of the inactive liquid shall be just sufficient to saturate P totally, and this will be the limit of their application. The value which the ordinate of the right lines will then take will coincide with the constant value which the characteristic function acquires for the same inactive liquid in the first phase, in which the weight E of this liquid attains or exceeds the proportion of saturation of P.

Third Case.—For each value of the relation $\frac{E}{P}$, relative to a same inactive liquid, the weight P of the active substance forms one or more fixed combinations, the constitution and number of which remain invariable within certain limits of values of this relation; after which they change abruptly to form another system of analogous combinations, which remain similarly fixed within certain limits of $\frac{E}{P}$.

Then, in virtue of § 25, the characteristic function

$$\frac{\alpha(P + E)}{P l \delta}$$

varies by abrupt interruptions, assuming successively various values, each of which remains constant within certain limits of the relation $\frac{E}{P}$; at least this kind of variability should generally take place, and the succession of the constant values of the characteristic function should likewise be different in general when the nature of the inactive liquid changes. In each of the magnitudes of $\frac{E}{P}$, in which it remains constant, the state of the system becomes analogous to the second case of the phase of supersaturation, which has been discussed in § 21; only it varies by interruptions instead of remaining fixed for all the ulterior values of the relation $\frac{E}{P}$.

28. In conclusion, of the five presumptive kinds of physical constitution which the systems above considered may present, there are four the realization of which may be detected by optical laws observable experimentally. The only one which eludes these determinations is that in which the inactive liquid, being insufficient in quantity to saturate completely the weight P of the active substance present, would distribute itself equally among all the molecules of that substance, so as to form with it chemical groups imperfectly saturated and identical among themselves, but whose proportions would vary progressively according to the different values of the relation $\frac{E}{P}$. The existence of this exceptional case will be manifested by the special forms of variability, and exclusive of the four others, which the characteristic function $\frac{\alpha (P + E)}{P l \delta}$ will present; at least, admitting that the five forms above enumerated include all the cases of constitution of the mixed systems chemically supposable. If others were to be imagined, the optical effects which they should produce may be in like manner characterized theoretically, according to the definitions which we should assign to their state, and the observation of the effects really produced would show if the supposed case of constitution were realized or not.

29. All the preceding conclusions, as well as the reasonings from which they are derived, suppose essentially that the deviations impressed on the planes of polarization of the luminous rays, under the circumstances in which they are applied, are *solely* produced by a molecular action proper to the constituent groups of the media observed, considered as being in an absolute state of disaggregation; so that the polarized ray be solely influenced by the power of deviation which they successively exercise upon it, independently of one another. It becomes then indispensable to specify the physical tests by which we may ascertain that this condition of independence is or is not fulfilled, or only incompletely. For these three cases occur in the experiments, and we should arrive at very erroneous results if we did not distinguish them before applying the formulæ above established. I proceed, therefore, to assign them special characters in the following paragraphs.

30. To make a legitimate use of the formulæ established in the foregoing paragraphs, we must be assured that the deviations

of the planes of polarization, to which we apply them, are produced solely by the individual action of the chemical groups which constitute the bodies in which they are observed, without the actual state of aggregation of these groups exercising any influence, either by modifying the optical power which they would exert if they were isolated, or by producing in their union effects of polarization which would imitate those, or would mask them by combining with them. These specifications are indispensable; for experience shows that phænomena of deviation, analogous or similar to the eye to those above defined, may be produced in systems which do not act molecularly. But then they result from the natural or artificial mode of apposition which the sensible parts composing these systems have amongst themselves, and they no longer take place when disaggregated. On the other hand, material molecules, which, disaggregated, appear individually active, may be grouped so that the phænomena of polarization, produced by their union, conceal or render insensible the effects of their proper power, although it continues to be exerted. These various cases proceed evidently from the conditions, purely molecular, supposed by our formulæ; we must therefore be acquainted with their existence, and be able to recognise them, in order not to apply to them erroneously a theory adapted to quite another class of facts.

31. For example; when a plate of quartz, regularly crystallized, is cut perpendicularly to the axis of the crystals, if a white luminous ray, previously polarized in a single direction, be passed through it normally, the planes of polarization of this ray, after its emergence, are deviated from their primitive direction, and unequally for the elements of unequal refrangibility. This fact was discovered by M. Arago in 1811*. On studying it a long time after, at various times, I found the following experimental laws for it. In all the regular plates, cut from the

* M. Arago published this fact in a memoir inserted among those of the class of the physical and mathematical sciences of the Institute of France, for 1811, part 1. p. 93. This investigation is entitled "*Mémoire sur une modification remarquable qu'éprouvent les rayons lumineux dans leur passage à travers certains corps diaphanes, et sur quelques autres nouveaux phénomènes d'optique.*" My first researches on the rotatory phænomena observed in the plates of crystallized quartz, perpendicular to the axis, were two years later. They were published in the same collection for 1812, part 1. p. 218, but were only completed in a later memoir, inserted in vol. ii. of the Collection of the Academy of Sciences, p. 41.

same crystal, the deviation of the plane of polarization of one and the same simple ray is proportional to the thickness; and, for rays of different refrangibilities, this deviation, through one and the same thickness, is sensibly reciprocal to the squares of the lengths of their fits, and therefore increases with the refrangibility. Lastly, the direction of the deviations is constant for all plates taken from the same mass regularly crystallized; but it is occasionally different in different crystals, being in some directed toward the right of the observer, in others towards the left, with the same general laws of dispersion, as well as of absolute intensity. This opposite action is even frequently observed in different parts of a plate cut from the same crystal. But then these portions are always limited by planes parallel to the faces of the hexagonal prism; which shows that these planes are faces of junction, by which the crystals possessed of contrary actions have become invisibly joined with one another, to form one total solid prism. All these peculiar effects, when merely the normal incidence is taken into consideration, are similar to those observed through liquids which deviate the planes of polarization of luminous rays. There is no difference except in the absolute magnitude of the deviations with equal thickness, and in their relations for the rays of different refrangibility. Again, with respect to this last circumstance, if we except tartaric acid, which in its solutions by various liquids, and in several combinations into which it may enter, disperses the planes of polarization of the various colours according to different laws from other active bodies, all these act so nearly like rock crystal, that, when the absolute deviation has been rendered equal for a single one of the simple rays, by varying the thickness, the tints of the two images developed by the double-refracting prism in all its positions around the transmitted ray, appear identical in equal azimuths, and we can only ascertain differences by very delicate processes of opposition. Nevertheless, from these analogies alone we could not legitimately infer that the action exercised thus by the rock crystal on polarized light is molecular. To attribute this character to it, we must prove that the same phænomena are likewise produced by the constituent elements of the crystal, that is to say by silicic acid in the state of disaggregation. Now, all the experiments tried with this view give negative results. Thus quartz fused

artificially, or liquefied in its combination with potash, becomes inactive, even when care is taken to form the combination with portions of the same crystal acting in one and the same direction, as Sir John Herschel has done. Quartz *résinite*, opal, *tabasheer*, opaline quartz of Mexico, some specimens of which present the most perfect limpidity, are also devoid of rotatory power, although these substances are composed of silicic acid, like rock crystal, from which they only differ by the absence of crystallization, and probably by a greater or less amount of combined water. To reconcile these facts with the supposition that the double power exercised by crystallized quartz was molecular, we must admit first that the silicic acid exists in it in two different states, of which we have no proof; for that would be necessary to explain the occasional alternation of the deviations toward the right or left of the observer. It would moreover be necessary that artificial fusion, as well as all the natural causes which destroy crystallization, should also destroy this dissimilarity, and reduce the acid to an inactive state, without its ever again acquiring its power in any of the combinations into which it might be made to enter, which would form a single exception to all the analogous cases. It is far more probable that the rotatory properties of the crystallized quartz result from the mode of superposition of the crystalline laminæ composing the crystals, which, when broken transversely, always present an helicoïdal structure, arranged around the longitudinal axis passing by each of their internal points. This would explain why the optical effects thus produced are especially regular in the central portions of the plates, situated near the principal axis of the crystals; whilst towards the outer edges, where the continuity of the crystallization has been modified by the lateral causes limiting it, they generally appear irregular and of variable intensities, even becoming sometimes completely evanescent. We might thus again conceive how crystals possessing contrary rotations may have been agglutinated laterally, in a simultaneous formation, so as to furnish transverse plates presenting this opposition in the different portions of their surface, with alternations sometimes infinitely multiplied, as in the variety of quartz called amethyst; whilst so varied a dissimilarity of molecular state would be incomprehensible in such à simultaneity and proximity of development. Lastly, what confirms the foregoing inductions is, that according to a remarkable observation due to Sir John

Herschel, in all the needles of crystallized quartz whose lateral faces present triangular facets, directed obliquely to the axis, —a peculiarity which characterizes the variety called *plagihedral*,—the direction of the rotation, in the vicinity of these facets, is in constant relation to their direction; so that, like them, it must be an accidental result of the mode of grouping of the constituent molecules, and not a quality individually peculiar to them*.

Although the justness of this consequence does not require that we should know how similar effects may be produced by

* I possess two needles of rock crystal which present the very rare peculiarity of having plagihedral facets in opposite directions. Nevertheless, the plates perpendicular to the axis, which I have cut from them in the different portions of their length, have presented, in each crystal, a rotatory power of the same direction and of a constant energy. This energy appeared to me, moreover, not to differ from that which is found in other plates of the same mineral, when they are examined at some distance from their edges, where the uniformity of opposition of their laminæ is generally disturbed by the influence of external causes, which have arrested their transversal development and have placed a limit to it. But this observation does not destroy the reality of the relation observed by Sir John Herschel between the direction of the plagihedral faces and the direction of the rotatory action, when it is restricted to the specifications which he himself has assigned; for, in studying it in plates of amethyst, where the direction of the action is almost infinitely varied, he observed that the connection in question exists only, as a constant and general fact, for the transversal portions of the plates which are nearest to each plagihedral face; without our knowing why it takes place, why it ceases, or how far it may extend. If the reader wishes to know the elements of this discussion more in detail, he may consult Sir John Herschel's memoir, inserted in the Philosophical Transactions of Cambridge for 1820, or the *Comptes Rendus de l'Académie des Sciences*, for the first *semestre* of 1839, vol. viii. p. 683. We need only remark that the English philosopher had considered it correct to invert the significations of the assertions and signs which I had previously given to the two directions of the deviations; so that, instead of writing them as being produced toward the right of the observer ↗, or toward his left ↖, *as they are seen*, he writes them *as they are not seen*, placing the observer astride on the luminous ray, in a position opposed to his real position. This mode of statement, which would create continual chances of error in the transcription of the experiments, has been maintained in the general treatise of the same author on light; so that he attributes to the small number of active liquids, which I had up to that time observed, directions of deviation the inverse of those which I had assigned them. Other English philosophers have adopted the denominations imagined by their countryman. But as none of them, not even Sir John Herschel, have added, as far as I am aware, any new observation to those which I had made, the direct mode of statement which I had introduced, and which I have continued to follow, has, I hope, generally prevailed. When the author of a discovery in physics has given a simple and faithful statement of it, which expresses its sensible characters, and which enables us to describe their applications without risk of error, it would be just, and scientifically convenient, not to change that statement without serious motives; above all, care should be taken not to change it for a worse, when nothing new is added to the facts which it comprises.

suitable aggregations of material elements individually inactive, the possibility of imitating them thus artificially would add much to its force. Now this is what Fresnel has effected by submitting a ray, polarized in a single direction, to the action of a thin lamina of gypsum, comprised between two rhomboids of glass, in each of which this ray undergoes internally a total reflexion; the first before traversing the thin lamina, the second after having been modified by it. For on varying the constituent pieces of this apparatus, according to the conditions which the theory of undulations had suggested to him, he succeeded in impressing on the transmitted ray modifications exactly similar to those which an assigned thickness of essence of turpentine produces, not only for the direction of the deviation, and for the nature as well as the apparent order of succession of the tints in the different azimuths of the analysing prism, but also for the law of dispersion, in the inverse ratio of the squares of the lengths of their fits, which experiment had previously established as an almost exact approximation in all the active substances hitherto observed. It was then unknown that this identity of dispersion of the planes of polarization was not completely exact; and above all, that tartaric acid dissolved in inactive liquids totally destroys it. But, if these remarks take from the apparatus of Fresnel the generality of theoretical application which he supposed it to possess, as reproducing a relation of dispersion which would have been inherent in the nature of the luminous principle, the particular imitation which he gives of that which is observed in the essence of turpentine, and consequently in rock crystal which follows a similar law, proves that there is no physical impossibility in the rotatory power of this crystal in the direction of its axis being an effect of aggregation, and not a molecular effect, as all the other circumstances related above agree in indicating.

32. When a plate of rock crystal, perpendicular to the axis of the crystal, is traversed normally by a luminous ray polarized in a single direction, the power of double refraction, resulting from the uniform crystallization, is null on a ray thus circumstanced, and cannot change the direction of its primitive polarization. Therefore, as such a change is then actually produced, it must necessarily result from an accessory cause, which, as we have just observed, resides, in all probability, in the mode of apposition of the crystalline laminæ constituting each crystal. Whatever it may be, let us abstract it for a moment, and consider only the effects of the double refraction with a single

axis, which is inherent in the general construction of the crystal. Let us then leave the normal incidence, and incline progressively the plate on the polarized ray, keeping always the plane of its faces perpendicular to the plane of primitive polarization. The transmitted ray will become oblique to the axis; and if it were composed of natural light, it would undergo internally double refraction. But being wholly polarized in the plane of incidence, which likewise contains the axis, it escapes this effect, and should be transmitted undivided, undergoing ordinary refraction, which preserves to it its direction of primitive polarization, since it coincides with that which this refraction tends to give it. These results of the general theory may be observed through all plates of uniaxal crystals cut normally to this line, and they are there realized very exactly. But they are quite different in plates of rock crystal perpendicular to the axis of the crystals, from the intervention of the rotatory power, which is exerted simultaneously with the general double refraction of which it is independent. For first, under the normal incidence, where this power acts alone, the whole of the transmitted ray is modified by it. In fact, if, after its emergence, it is analysed by a double refracting prism, having its principal section parallel to the plane of primitive polarization, this ray, instead of passing through simple, under the sole influence of ordinary refraction, is broken into two distinct portions differently coloured, one of which, O, follows the ordinary refraction; the other, E, the extraordinary refraction, forming images similar in colour, as well as in relative intensity, to those which would be observed in the same position of the analysing prism if the same ray had traversed a certain thickness of a colourless, active liquid. But, under oblique incidences, the phænomena become very different for the liquid and for the crystal. When the stratum of liquid is progressively inclined, preserving it perpendicular to the primitive plane of polarization, the two images, O, E, change colours and relative intensities, from the increase of length of the course of the ray among the active molecules. When the same experiment is made with a plate of rock crystal perpendicular to the axis, the image E again varies, *as to its tint*, conformably to the same rule. But its relative intensity decreases more and more in proportion as the inclination increases; and the rays which it abandons, being transferred into the image O, recompose there a white more and more abundant with the proper portion of that image which is complementary to them, and which weakens by so much its

colour. Lastly, beyond a certain inclination, which varies with the thickness of the plate, the portion of light contained in the image E becomes insensible, and the whole of the transmitted light appears to have passed into the image O, as if the rotatory power had disappeared. But the progress of the phænomenon proves that it continues to exist even then, and that its influence has only become too weak, relatively to the increasing energy of the double refraction, to remove from the latter an appreciable portion of the transmitted light. This division of the interior ray between two powers of polarization distinct in their cause, and in the laws, both absolute and relative, of their action, would doubtless be a very curious phænomenon to study. For the unequal susceptibility which it indicates among the elements of the same luminous ray, to yield to or escape from one or the other action, appears to be connected with their most intimate nature.

33. But the foregoing fact already warns us that the molecular rotatory power can only be observed in solid bodies, under certain conditions, dependent on the mode of aggregation of their mass. If this mass is not crystallized, nor stratified in distinct layers among which special phænomena of polarization are developed, the rotatory power proper to the chemical groups which constitute it are indistinctly manifested in all directions, with the peculiarities of direction and of energy which belong individually to those groups, in the physical state in which they then are. If, on the contrary, the mass is regularly crystallized, its internal structure will be symmetrical around a point, a right line or a plane. Let us admit, moreover, that no effects of *lamellar polarization* are there developed, which disguise or conceal those which we now wish to consider*. Then, in the case of sym-

* This class of phænomena is observed in certain crystallized bodies whose masses are formed of distinct layers, stratified in continuous systems, where they are respectively parallel. Each of these systems produces effects upon polarized light in part analogous to those of piles of glass plates, but which are related by other characters to those of crystalline laminæ, possessing double refraction. They are, however, independent of this latter property, for they have hitherto been observed solely in bodies which are deprived of it. If it may occasionally exist in combination with them, which is very probable, it must render them more difficult to be perceived, by impressing on the polarized light different directions of polarization, and more energetically established or more fixed, which would weaken their proper effects, or entirely conceal them. They may, without doubt, be likewise associated with the rotatory power in solid crystallized bodies, although they have not hitherto been observed in such a state. For this reason I have comprised this physical possibility in the general statement of the circumstances which may mask the rotatory properties. If the reader desires to know in detail the phænomena produced by this kind of polarization, which I have called *lamellar*, he may consult vol. xviii. of the *Mémoires de l'Académie des Sciences*, in which I have expounded them.

metry around a point, the rotatory power proper to the constituent particles will manifest itself freely and with a uniform energy in all directions, as in the state of disaggregation. If the symmetry takes place around a right line, the crystal will exercise uniaxal double refraction, which will be the right line itself. Then the rotatory power proper to the constituent molecules will not be exercised freely except in that single direction; and it will be especially there that we must seek to detect its manifestation. But, since the crystallization will there maintain all the molecules in parallel directions, the total rotatory power resulting from them collectively may possibly be found different from what it would be in the state of disaggregation or of confused aggregation, which would present them indistinctly turned in all directions around the transmitted ray. Lastly, in the third mode of symmetrical crystallization around a plane, the body will exercise binaxal double refraction, according to which we must consequently endeavour, by analogy, to ascertain the phænomena of molecular rotation, if this system of double refraction, in which the transmitted ray is always oblique to one of the two axes, allows them to be manifested; and the parallelism of the constituent molecules might very well, in this case also, produce total resultants different from what they would be if these same disaggregated molecules could present themselves in any direction whatsoever to the luminous ray passing through them, or if, remaining aggregated in a solid system, they were there disposed according to a mode of arrangement which had nothing regular.

34. This last state—that of confused aggregation—is the only one in which the rotatory power of a solid body has hitherto been observed with the uniformity of agglomeration necessary to measure its energy, and to compare it to the action of the same body disaggregated by solution in an inactive liquid. The substance which has furnished the example is cane-sugar, deprived of crystallization by fusion, and then solidified by rapid cooling.

In order to obtain it in transparent masses, it is first dissolved in a small quantity of water; and the solution being well-clarified, a little acetic acid is added. This solution is then brought over the naked fire to the consistence of a syrup, sufficiently dense that threads drawn from it solidify immediately. It is then poured into metallic cases with very thin sides, on a cold marble slab, where it immediately solidifies into diaphanous plates, generally of a yellowish tint, the less intense the less it was heated, and they are sometimes obtained nearly colourless; this

is what is commonly called *barley-sugar*. These plates, traversed by a polarized ray, exercise upon it the rotatory power, with an energy in each case proportioned to their thickness, or as they interpose a greater total thickness in the course of the ray, when placed one after another. This power is directed towards the right of the observer, like that of the primitive sugar in solution in water. To render the observation exact, I poured out the syrup and cooled it briskly in a little rectangular vessel terminated by thin glass sides with parallel faces, the intervals of which had been carefully measured in the two directions of the rectangle*. The deviations produced on the same simple ray are found exactly proportional to the thicknesses which these intervals comprise, as the apparent homogeneity of the mass would lead us to presume. The absolute valuation of the power of this mass required the knowledge of its density. In order to obtain it, I filled with the same solidifiable syrup a small phial, having first ascertained its weight and that of the water which it contained at a known temperature. Having then weighed it again, after this solidification, and deducted its own weight, the remainder compared to the weight of the water gave me the density of the solid syrup, which I found to be 1·5092. With this number taken for δ, and the deviations α observed *on the red ray* through the thicknesses l, I calculated the molecular power of the solid mass on this same ray, by the formula (1.) of § 8; and calculating it for 100^{mm}, I found

$$[\alpha]_r = \frac{\alpha}{l\delta} = +\,42^{\circ}{\cdot}568.$$

This being done, I took a known weight P of this same sugar, and dissolved it in nearly an equal weight E of distilled water, so that its ponderable proportion ε in the solution was 0·50075. The density δ of the mixed system thus formed was found to be 1·22676. With these numbers, and the deviation α produced by this system *on the red ray* through a tube l of a known length, I calculated the molecular power of the dissolved sugar by the formula (2.) of § 14, *considering it as in the state of simple mix-*

* The experiment to which I here refer is given in my *Mémoire sur la Polarisation circulaire*, inserted in tome xiii. of the *Mémoires de l'Académie des Sciences*, p. 128 *et seq.* The numbers are the same as I employ here, only they are there discussed in an inverse manner. At page 119 of the same memoir will also be found the experiments on solutions of pure cane-sugar, mentioned in the subsequent part of the reasoning. I avail myself of this occasion to correct the error of a word at page 131 of that memoir, line 10 from the bottom: instead of *plus fortes* read *plus faibles*.

ture in the mixed system; and the calculation, made as above for a thickness of 100^{mm}, gave

$$[\alpha]_r = \frac{\alpha(P+E)}{P l \delta} = +44^{\circ}\cdot 359.$$

Considering these experiments as perfectly exact, we should conclude that the sugar here investigated combines with a certain proportion of the water in which it is dissolved, and to which it communicates the rotatory power; so that the mixed group thus formed would be specifically a little more energetic than the primitive solid group. Several circumstances independent of the foregoing tend to confirm this induction. For, first, the solid sugar thus obtained strongly attracts moisture from the air, and becomes deliquescent; and by this absorption, radiating centres of crystallization are formed in the interior of the mass, which quickly destroy its transparency when left thus exposed. These modifications, resulting from its affinity for water, should therefore be immediately produced when dissolved in this liquid. Moreover, having formerly observed aqueous solutions of the same crystallized cane-sugar, where I had introduced this sugar in various proportions by weight, from 0·25 up to 0·65, the specific rotatory power $[\alpha]_r$, calculated by the function $\frac{\alpha(P+E)}{P l \delta}$, was found to be progressively somewhat higher in those in which the proportion of water was greater, which is also in agreement with the foregoing results. Nevertheless, I am not inclined to offer these analogies as absolutely decisive, because the experiments on which they are founded are of ancient date, and perhaps less minutely accurate than they might be made at the present time with this special object. But I shall bring forward others more numerous and striking, in which the same physical result, that is to say the communication of the rotatory power to inactive liquids by an active substance dissolved in them, will be clearly evident.

35. The rotatory power of pure cane-sugar, calculated according to its aqueous solutions for the red ray, and for a thickness of 100^{mm}, appeared to me, as the mean of several experiments, to be

$$[\alpha]_r = 54^{\circ}\cdot 762.$$

It is therefore considerably stronger than that of the same sugar decrystallized by fusion just considered. To ascertain to what this difference is attributable, I prepared some new plates of the decrystallized sugar, and having dissolved them in water in a known ponderable proportion, I submitted the solution to the test of inversion by hydrochloric acid, to ascertain the propor-

tion of crystallizable sugar it might contain, and to see whether it was associated with other non-intervertible sugars, but gifted with the rotatory power towards the right or towards the left, which would have been modified during the operation*. I found that in fact a considerable portion of the primitive sugar had remained unaltered, for it amounted to 0·92 of the weight of the total mass of the sample examined. But the remainder of the mass with which it was associated was deprived of rotatory power. This last result agrees with an experiment of M. Mitscherlich, by which this philosopher ascertained that cane-sugar, heated to 160° in a bath of chloride of zinc, is transformed into an inactive body, at the same time preserving its transparency. This undoubtedly is the modified portion of the total mass, which, interposing itself between what remains of the crystallizable molecules, and solidifying with them by the effect of quick cooling, hinders them from grouping in crystals of sensible dimension, and allows the resultant of their individual molecular powers to be perceived. This resultant will therefore be the greater the less the heat employed, which was the case with the experiment which I have mentioned; for it had been arrested as nearly as possible at the term necessary to obtain non-crystallized diaphanous plates. But it will be conceived that a more lively or longer continued action, by neutralizing a greater proportion of the sugar employed, should give masses possessing a less rotatory power; this was the case in the first experiment above related. For, on applying the same principle, and considering the mass then obtained as composed of unaltered crystallizable sugar, associated with a neutral system, we find that the ponderable proportion of this sugar, calculated from the aqueous solution, was only 0·81†.

* The detail of this process, as well as the formulæ necessary for its application, have been given in the *Comptes Rendus de l'Académie des Sciences*, tome xv. pages 528, 534, 697 *et seq.* The reader may also see in the same collection, tome xvi. p. 619, the manner of employing them for the quantitative analysis of the solid or liquid mixtures in which crystallizable cane-sugar is associated with other non-crystallizable sugars. The progressive course of the inversion produced by various acids has been considered comparatively in tome xvii. p. 755. The effects are there described which they produce according to their nature, the proportion employed, the temperature, and the time during which they are allowed to act.

† This is seen from the formulæ established in the *Comptes Rendus de l'Académie des Sciences*, tome xvi. pp. 619 *et seq.* Let x be the ponderable proportion of crystallizable cane-sugar contained in a solid mass, composed of this sugar associated with other non-intervertible sugars, exercising the rotation towards the right or the left, and with any system of inactive bodies. A certain weight, p, of this mass is dissolved in a known weight, e, of distilled water,

36. The turpentines which produce deviations of constant direction when liquefied by heat, and then restored by cooling to a viscous state, in which their sensible parts are almost deprived of relative movements, may also be presented as an example of bodies which exercise the rotatory power in the solid state; for the condensation which the cooling produces, increasing this power for an equal thickness rather than weakening it, it cannot be doubted that they would preserve it if they were submitted to an artificial temperature sufficiently low to solidify them completely; and the natural temperature of our winters already suffices to harden them considerably without their action being destroyed or apparently weakened. These facts, and those still

and the solution, having the density δ, is observed in a tube of the length l, where it produces in the red ray the deviation α. If $[\alpha]'_r$ be called the molecular power of the primitive mass upon this same ray, and we make for the sake of abbreviation

$$\varepsilon = \frac{p}{p+e},$$

we have, by the equation (2.) of § 14,

$$[\alpha]'_r = \frac{\alpha}{l\varepsilon\delta}.$$

Now, by the experiments of inversion explained in the article cited in the *Comptes Rendus*, the portion S of the deviation α which is produced by the intervertible and consequently crystallizable sugar, which the mass experimented on contains, is determined. Then, designating by $[\alpha]_r$ the proper rotatory power of this sort of sugar, on the red ray,—a power previously determined by direct experiment,—the formulæ cited give

$$x = \frac{S}{\alpha}\frac{[\alpha]'_r}{[\alpha]_r}.$$

Let us imagine that the crystallizable sugar contained in the proposed mass is there solely united with inactive substances; then the observed deviation α being produced entirely by this kind of sugar, the experiments of inversion should give $S = \alpha$; and, by this equality, they will prove that the circumstance in question takes place. We shall then have in such a case

$$x = \frac{[\alpha]'_r}{[\alpha]_r}.$$

I have stated that the preceding condition $S = \alpha$ was sensibly realized in the experiments of inversion which I made on plates of sugar decrystallized by heat. Admitting then that such was the case in the first experiment which I related, where the active mass had been prepared in the same manner, excepting the more lively or more prolonged application of heat, the second expression of x will be applicable to it; and on introducing the numbers respectively given for $[\alpha]'_r$ and $[\alpha]_r$, we deduce $x = \frac{44{\cdot}359}{54{\cdot}762} = 0{\cdot}81$, that is to say, it should contain $\frac{81}{100}$ in weight of unmodified crystallizable sugar, as I have stated in the text. In fact, treating this mass by the process of refining, a considerable quantity of candy-sugar in crystals is obtained; but the exact proportion of this sugar could be appreciated only by the experiments of inversion, because in the operations employed to extract it materially, a considerable quantity is always lost, both by destruction and by mixture with non-crystallizable residues.

more evident which I have just related respecting decrystallized cane-sugar, prove therefore that the solid state is by no means incompatible with the exercise of the rotatory power, as very distinguished philosophers had supposed it to be, against all probability, when these phænomena were first discovered*; but, as I have stated, they may be rendered less sensible, or completely masked, by the more energetic phænomena of polarization which crystallization developes when it accompanies solidification. For example, I have never been able to observe traces of it in the most transparent samples of solid camphor, although this same camphor acts with much energy when dissolved in alcohol, or liquefied by heat, and brought to the state of ebullition. But it is likewise easy to demonstrate, on studying the action of the solid camphor on polarized or non-polarized light, by the modifications which it produces, that the smallest fragments of this substance, apparently the best-crystallized externally, are internally only confused assemblages of an infinity of small crystals turned in all directions, so as to constitute veritable *macles*; we ought not therefore to be surprised if the proper polarizing action which these crystals exercise individually, mask the much weaker effects of the rotatory power of the particles composing them.

I have sometimes imagined that I perceived traces of these molecular effects on the directions of the axes of the crystallized cane-sugar, but I have not been able to procure pieces sufficiently large and pure to render this result certain. I have vainly attempted also to obtain tartaric acid fused into transparent and solid masses, to make with it the same observations. They would, moreover, have had another kind of interest; for the rotatory power of this acid in its aqueous solutions diminishes at an equal temperature, in proportion as the water present is

* This idea was broached by Sir John Herschel in his 'Treatise on Light,' § 1046, and it has been reproduced without observation in the translation of that work published at Paris; I cannot therefore pass it by in silence, coming as it does from so distinguished a philosopher. Sir John Herschel objected that neither solid camphor nor crystallized cane-sugar, observed in the direction of one of its axes, manifested any rotatory power, whilst, on the other hand, crystallized quartz, which exercises this power in a solid state, ceases to manifest it when fused by heat or combined with potash. But the considerations which I have now given very well account for these facts. In the solid camphor, and in the crystallized cane-sugar, the crystalline state developes polarizing actions whose energy masks the effects of the rotatory power, by depriving them of the light on which they should act. In quartz fused or disaggregated by combination with potash, rotatory action is no longer observed, because it was not there molecular. It was a result of its lamellar constitution which the disaggregation has destroyed.

decreased; and as it cannot be liquefied by heat without removing from it, at least temporarily, a portion of its constituent water, it is impossible to tell whether, after cooling and solidification, it would preserve an appreciable rotatory power. But it would recover it, undoubtedly, on recombining with the water, or even without a complete restoration of that liquid, if it was again liquefied by heat alone, as this considerably increases its power. And, in fact, I have found it to be very energetic on observing it thus, in the state of fusion, before spontaneous solidification. If we compare these results with what I have said in § 11 respecting the temporary modifications which the molecules of this acid experience under the influence of heat, it will, in my opinion, be regarded as highly probable that this influence, combined with that of the proportions of water added or removed from it, converts it into so many different bodies; and that this continued mutability is the cause of the diversity of the chemical affinities which it has been found to possess, in the small number of terms of its progressive transformations in which we have been able to observe it in the state of definite combination.

37. We shall subsequently see this singular acid manifesting, in its action upon polarized light, special properties which result from the two principles of modification which I have just indicated. But before studying it by the optical characters which it produces in the combinations into which it enters, and concluding from them the fixed or variable nature of these combinations, by the formulæ established above, I shall first prove the legitimacy of their applications, and confirm all their general consequences, by the employment of a different class of physical facts, which I have not employed to establish them, and which agree completely with them in their results.

Addition.

Whilst the foregoing portion of this memoir was in the press, I attempted to effect the complete solidification of the turpentines, with the object explained in § 36. I repeated that experiment twice; and, although accessory circumstances, which intervened in the results, prevented their being perfectly suitable to the object proposed, they presented other characters sufficiently curious to merit being described.

I first experimented on the kind of turpentine, the rotatory effects of which are mentioned in § 5. It was still in the same rectangular box in which I had measured them at the temperature

of 7°·5, and I moreover filled a small test-tube with it. The whole was placed in a freezing mixture, composed of crystallized chloride of calcium and snow, the temperature of which fell lower than 35° below zero. After remaining there sufficiently long, the test-tube was withdrawn; then, having ascertained through its sides that the matter which it contained still exercised an action upon the polarized light, but whose direction and energy were not sought to be determined, it was broken with a hammer, and I found the inclosed mass broken into fragments perfectly solid, similar in appearance to barley-sugar or to solid resin. This being ascertained, the rectangular box was withdrawn, and I sought to observe through its sides the power which the internal mass which had remained transparent exercised. I found it still in the same direction as in the semi-fluid state. But it was evidently modified by the phænomena of polarization analogous to those which annealing produces in glass; and it was unequally so in the different portions of its entire mass. As the layer of congealed vapour which was deposited incessantly upon the external layers of the box destroyed their transparency, and might even have interfered with the results, these sides were well-cleaned before the observation. Now, after one of these frictions, a kind of sudden cracking was heard, which made me think the box was broken; but it was only an internal movement of the inclosed substance, which immediately became opake and traversed by a thousand fissures.

In proportion as it commenced to reacquire the external temperature, the transparency reappeared, and with it the rotatory power. This restoration took place, as was to be expected, at first near the external surfaces, which showed that the central mass, still solid, consisted of a kind of nucleus bristled with an infinity of very long needles, absolutely similar to those which are developed in many substances when they crystallize. The same phænomena of sudden cracking, followed by a breaking-up and opacity, and then by partial fusion with crystalline structure, were again reproduced in a second experiment, in which the same kind of turpentine was submitted to a cooling rather less intense. M. Regnault suggested to me that it would be interesting to profit by the inequality of the fusion to endeavour to isolate the portion of the mass which solidifies in the form of needles, because, probably, a definite product might thus be extracted from it. I merely mention this ingenious idea, however, which other experimentalists will be better able to realize.

In the second experiment I submitted to the same test of cooling another variety of turpentine, which also exercised the deviation towards the right in its primitive state, but with a less energy than the preceding one. It attained also with much greater difficulty complete fusion when heated to the same degree; and both by this want of relative mobility and by its own nature, it appeared to conduct heat much worse. This variety did not present any of the phænomena of sudden solidification which I have just described. I do not even think that the mass ever became solid in the interior; for, on uncorking the flask in which it was contained, and trying the state of its surface with a cold metallic point, I found it to have the appearance of a solid crust which might be scratched and reduced to powder; but on pressing it, the mass yielded, as if it had been preserved from cooling and solidification by this external envelope. It is perhaps by a consequence of the same fact, that the deviation effected by the total mass appeared sensibly the same as previous to its being placed in the freezing mixture.

I availed myself of the same occasion to study the effect of cooling on some other substances. Some very thick syrup of dextrine, submitted to a temperature which was certainly below $-35°$, in a very small flask, preserved its gummy state without solidifying, Another more aqueous sample froze completely, and became of a dull white, like snow; but after spontaneous melting, it had lost none of its power. A syrup of cane-sugar, acted on by hydrochloric acid, and then neutralized with perfectly pure marble, solidified easily. After resuming its liquid state, it exercised the deviation towards the left, as previously. However, according to a remark made by M. Soubeiran, the accuracy of which I have confirmed, when this same altered sugar solidifies *by crystallization*, it acquires a rotatory power toward the right, as I observed in grape-sugar; and from that time the liquefaction in water, even united with the most energetic acids, no longer deprives it of this direction. Thus the act of solidification alone did not suffice to modify the altered sugar. as its spontaneous crystallization would have done. It would be interesting to ascertain if this difference in the results is peculiar to it, or if it be due to the presence of the chloride of calcium with which it was associated.

[To be continued.]

Fig. 1.

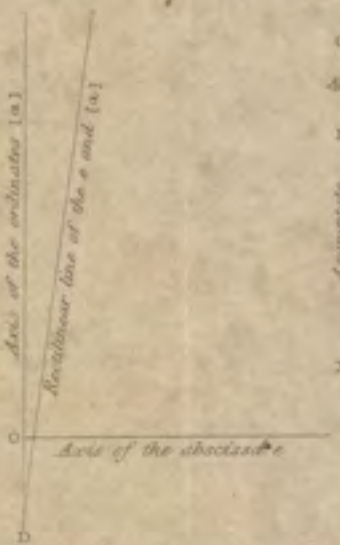


Fig. 2.

Fig. 8. Ternary systems where $e = 5\,E$.

Fig. 7. Ternary systems where $e = 3\,E$

Fig. 6. Ternary systems where $e = E$ in 346.

Fig. 4.

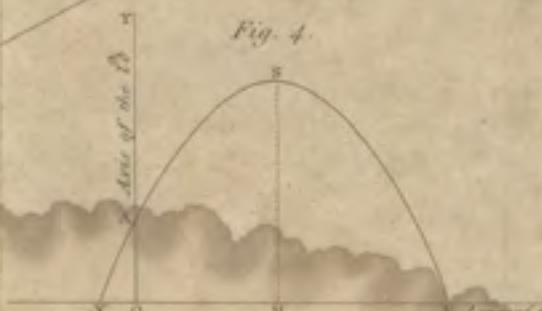


Fig. 3.

Fig. 5.

Fig. 5. relates to the combinations of tartaric with boracic acid and water.

Biot on the Employment of Polarized Light.

Fig. 4.

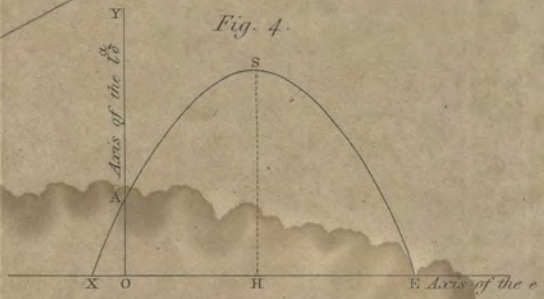


Fig. 5.

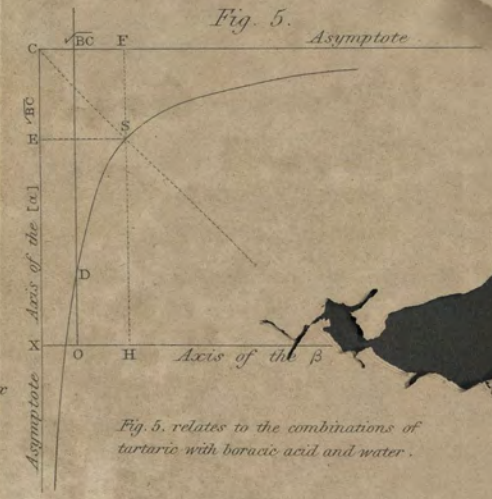


Fig. 5. relates to the combinations of tartaric with boracic acid and water.

d. Light.

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SCIENTIFIC MEMOIRS.

VOL. IV.—PART XV.

ARTICLE XII. continued.

On the Employment of Polarized Light in studying various questions of Chemical Mechanics. *By* M. BIOT.

SECTION II.—*On the relations which exist between the densities of mixed systems, and those of the partial systems which constitute them at a constant temperature. Agreement of these relations with the resultants of the action exercised by these different systems on polarized light.*

38. WHEN pursuing a path of research so novel and so mysterious as that on which we are now engaged, we must avail ourselves of all the aids which may throw any light upon it. With this view I shall fortify the deductions drawn above from the optical characters, by mentioning a class of facts of a wholly different nature which agree with them completely.

When a constant weight P of an active substance is associated with a variable weight E of an inactive liquid, without these two bodies decomposing each other, if the mass E is just sufficient, or more than sufficient, to saturate completely the affinity of P for it, we have established in §§ 14 and 27 that the function $\frac{\alpha(P+E)}{Pl\delta}$ must remain constant in all the mixed systems, constituted with any doses whatever of the liquid E, thus in excess. Now, under such circumstances, the chemical groups formed by the combination of P and of E being perfect, the quantities of E added in excess can no longer modify them. Therefore the syst[illegible] thus saturated should mix with the ulterior portions of E without either contraction or dilatation of volume, which may be proved by the comparison of their successive densities

observed at the same temperature. In fact it will be seen that this result is verified very exactly, in all the cases in which the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$ is constant.

On the other hand, if the inactive mass E is insufficient to saturate P, we have established in the same § 27 that the function $\frac{\alpha(P+E)}{Pl\delta}$ should be *generally* variable, from the diversity of the chemical groups formed in the mixed system according to the various doses of E, its remaining constant under such circumstances being an exceptional case. Thus, therefore, the different mixed systems which may be formed with P by successive additions of E, should *generally* be effected with contraction or expansion of volume; and this in fact takes place in the greater number of similar cases. This correspondence of variations, however, cannot be considered absolute; for experience shows that very energetic combinations may take place even between gaseous substances without contraction or expansion of volume. Now, it will be seen that this last condition is found occasionally to coexist with variations, not only in the values, but in the sign of the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$, which undoubtedly attests the successive formation of chemical groups of a very different nature.

39. To obtain the proofs here indicated, we must compose a formula expressing the density of a liquid system formed by the mixture, in whatever doses, of two other systems, which are supposed to mix without contraction or dilatation. Let

δ_1, δ_2 be the proper densities of the two liquids,

V_1, V_2 the mixed volumes of each,

P_1, P_2 the respective weights of these volumes;

lastly,

δ, V, P the density, the volume, and the weight of the resulting liquid.

The condition of the mixture proposed will be

$$V = V_1 + V_2.$$

Now the integral preservation of the composing weights, joined to the physical definition of the densities, gives

$$P = P_1 + P_2, \quad P = V\delta, \quad P_1 = V_1\delta_1, \quad P_2 = V_2\delta_2;$$

taking the expressions of the volumes V, V_1, V_2 in the three

last equations, and substituting them in the relation to which they are subjected, there evidently results

$$\frac{1}{\delta} = \frac{1}{\delta_1} \cdot \frac{P_1}{P_1+P_2} + \frac{1}{\delta_2} \cdot \frac{P_2}{(P_1+P_2)}; \quad . \quad . \quad . \quad (1.)$$

the second member is entirely composed of observable quantities. Its calculated numerical value will give therefore $\frac{1}{\delta}$, and consequently δ; that is to say, the resulting density in the hypothesis under consideration.

The coefficients of $\frac{1}{\delta_1}$ and of $\frac{1}{\delta_2}$ express respectively the proportions of the two liquids contained in each unity of weight of the mixed system. As their intervention is most usually indicated under this form in the tables of experiments which I shall use, I will introduce them explicitly, making for abbreviation,

$$\epsilon_1 = \frac{P_1}{P_1+P_2}, \qquad \epsilon_2 = \frac{P_2}{P_1+P_2};$$

whence will result

$$\frac{1}{\delta} = \frac{\epsilon_1}{\delta_1} + \frac{\epsilon_2}{\delta_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

to which must be added

$$\epsilon_1 + \epsilon_2 = 1.$$

If one of the liquids, for instance that to which the sign 2 is applied, is distilled water, in that case $\delta_2 = 1$, which supposes that the primitive density δ_1 and the resulting density δ are taken, comparatively with water, at a common temperature, in which the mixture formed has become stable. This community of temperature should also be supposed to occur, in the general case, for all the operations by which the three densities δ_1, δ_2, δ are evaluated, of which the equation (1.) expresses the mutual relations, whether measured relatively to distilled water, or to any other liquid taken as a type. The identity of temperature thus established allows of the formula being applied to each given case, and the result compared with experiment without any knowledge of the dilatations.

40. The expression of δ may even be applied to the case in which the element P_1 of the mixture is a solid body, provided that we know the density δ_1 which should be attributed to this body, when it is in a state of disaggregation immediately pre-

ceding its return to the state of solidity; whether, in this last state, it contains or does not contain water of crystallization which would solidify at the same time. Reciprocally, if this value of δ_1 was not known, it might be arrived at from the equation itself, for each solution in which ε_1, δ_2, and the resulting density δ had been observed directly; and we should thus find δ_1 constant, whatever were the amount of the solution on which we had founded our conclusion, provided it had always been made at a same temperature, and that it had been effected without contraction or dilatation, as the formula supposes. I shall adduce hereafter experiments of this kind.

41. I shall first apply the formula (1.) to the aqueous solutions of cane-sugar mentioned at the end of § 34, and the quantities of which are given in tome xiii. of the *Mémoires de l'Académie des Sciences*, p. 119. Since they gave for the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$, values nearly constant, but yet increasing a little with the proportion of water, we should expect that their densities would not exactly follow the relations proper to simple mixtures, but that they would deviate slightly. To these three solutions I have added a fourth, the quantities of which are given in the *Comptes Rendus de l'Académie des Sciences*, tome xv. p. 625. I have added the indication of the temperatures at which the densities were measured, and which I found registered in my note-book. Although these early experiments were made with only the ordinary care and precision which ought always to be used, and not with the refinements which might be employed for the special object which we propose here, I consider them as preferable, because they were not made with a view to this object. I shall subsequently relate more recent ones, which were made with the greatest care.

As all the saccharine solutions to be compared may be derived from one another by successive additions of distilled water, we must make $\delta_2=1$ in the equation (2.), and it then becomes

$$\frac{1}{\delta} = \frac{\varepsilon_1}{\delta_1} + (1-\varepsilon_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

Here δ is the density of the mixed system, in which the primitive solution, whose density is δ_1, enters in the proportion ε_1, the rest being water added or subtracted. Most frequently this proportion ε_1 is not given, and we only know the analogous proportion of solid sugar entering into the solutions compared.

To adapt the formula to these circumstances, without a new calculation, let us consider δ_1 as representing the density of the disaggregated sugar, supposed simply mixed with water in each solution. If δ_1 was known, δ would express the absolute density which this solution ought to have for the ponderable proportion ε_1. Designating then, by one or two accents, the various elements of two solutions made at the same temperature, but different in densities as well as in proportions, we have the following equations, in which δ_1 is common:—

$$\left.\begin{aligned} \frac{1}{\delta'} &= \frac{\varepsilon'_1}{\delta_1} + (1 - \varepsilon'_1); \\ \frac{1}{\delta''} &= \frac{\varepsilon''_1}{\delta_1} + (1 - \varepsilon''_1); \end{aligned}\right\} \quad \ldots\ldots \quad (2.)$$

then, on eliminating δ_1 between them, there remains

$$\frac{\varepsilon'_1}{\delta''} = \frac{\varepsilon''_1}{\delta'} + \varepsilon'_1 - \varepsilon''_1. \quad \ldots\ldots\ldots \quad (3.)$$

By means of this relation the density δ'' may be concluded from δ', according to the ponderable proportions ε'_1, ε''_1 of solid sugar entering into the two solutions under comparison; at least when it is admitted, as we do, that they are effected by simple mixture and at a common temperature, these two conditions being necessary for the constancy of δ_1. Reciprocally, in this same hypothesis, the value of δ_1 may be directly arrived at by the equations (2.) for each solution observed; and this value ought to be found constant, from whatever solution deduced, if they are associated by simple mixture.

The following table presents the application of these formulæ to the four solutions of cane-sugar above-mentioned. In the calculation of the successive densities I have derived the three last solutions from the first, in which the proportion of solid sugar was most considerable. Lastly, I have inserted in the last column the value of the density δ_1 of the disaggregated solid sugar, which would be concluded from each solution from its observed density and quantity, in the hypothesis of a simple mixture by diffusion.

Designations of the solutions considered.	Ponderable proportion of solid sugar contained in the unity of weight of the solution. ε.	Centesimal temperature at which the density has been observed.	Observed density, that of distilled water being taken for unit. δ.	Density derived from the first solution by formula (3.), on the hypothesis of a simple mixture.	Excess of observed density over calculated density.	Density of disaggregated sugar deduced hypothetically from formula (2.) for each solution. δ_1.
Mém., t. xiii. p. 118.	0·65064	+23°·75	1·31141	.....	.....	1·57472
	0·50055	.....	1·23109	1·22352	+0·00757	1·6003
	0·24999	.....	1·10525	1·10056	+0·00469	1·61618
Comptes Rendus, t. xv. p. 625 ...	0·571481	+18·00	1·26933	1·26353	+0·00580	1·59052

The numbers in the last column but one show that the observed density was always a little greater than the deduced density, as if a slight contraction had taken place when water was added to the solution most charged with sugar. The small inequalities of the numbers contained in the last column indicate the same fact, reproducing it under another form. These slight variations of densities agree therefore with those of the characteristic function $\frac{\alpha(P+E)}{P l \delta}$, not only in their existence, but even in their direction.

42. I have repeated the same experiments with syrup of cane-sugar, which I successively diluted with water in known proportions. Then the density δ of each mixed system, calculated in the hypothesis of a simple mixture, is deduced directly from the equation (2.), § 39, by making $\delta_2 = 1$, and designating by δ_1 the density of the primitive syrup observed without the addition of water. This formula, thus specialized, gives therefore

$$\delta = \frac{\delta_1}{\varepsilon_1 + (1-\varepsilon_1)\,\delta_1} \quad \ldots\ldots\ldots \quad (2.)$$

The following table presents the values of the densities δ thus calculated, and compared with the observations in the following experiments. All the densities were observed at the same temperature, 13° centigrade.

Ponderable proportion of the primitive syrup contained in the solution. ε_1	Centigrade temperature at which all the densities were observed.	Densities observed, that of distilled water being 1. δ.	Densities concluded from that of the primitive syrup, on the hypothesis of a simple mixture by the formula (2.).	Excess of the observed density over the calculated density.
1·00000	+13°	1·309733		
0·829083	+13	1·24649	1·24377	+0·00272
0·640603	+13	1·18235	1·17854	+0·00381
0·517879	+13	1·14331	1·13956	+0·00375

It is seen, by the numbers contained in the last column, that the mixed system has always experienced a slight contraction, which at first increased with the proportion of water added, after which it became nearly constant; for the diminution effected on the last decimal figure in the solution most charged with water, supposing it to be relied on, is a result connected with this very constancy. In fact, the excess of the observed density over the calculated density, must always end by becoming null when the quantity of water added becomes infinite compared to that of the primitive syrup with which it is mixed; and this is what the formula proves; since ε_1 being null, it then gives $\delta = 1$.

43. To complete these experiments, I determined experimentally the density of the crystallized cane-sugar, in order to compare it with the densities of this same sugar disaggregated, expressed by the last column of the first table in the hypothesis of a simple mixture, which, from the constant direction of its error, should give this density rather too high than too low. With this view, having chosen a specimen of oil of turpentine, which I intended to employ as a medium, I first conveyed into it some very minute fragments of candied sugar, the configurations of which I had carefully remarked; and I found that, after having remained for several days in this liquid, they underwent no appreciable alteration, even in their angular parts. I then partly filled with small isolated crystals of the same sugar, a specific gravity bottle whose weight I had previously determined, as well as the weight of the volume of water filling it at the temperature of 12° C., at which I operated. I took the weight of this mass of crystals; then I filled the flask with the essence of turpentine, taking care that no trace of air remained in their interstices, and I determined the total weight. I now emptied the bottle, and washed it several times with the essence, to remove all the particles of sugar; after which I filled it com-

pletely with this same liquid, the weight of which I measured. The latter, compared with the weight of the same volume of water, gave the density of the essence 0·87908; and the preceding operations made known the density of the solid sugar in relation to it: this latter was found to be 1·807937. The product therefore of these two numbers gives the density of the candied sugar compared to distilled water, which is thus equal to 1·58933. This value differs very little from those of δ_1 given in the last column of our first table, as being determined from the four aqueous solutions there considered. From this therefore it is evident that the sugar-candy, on the point of separating from water in order to solidify with the portion of that liquid which enters into its crystallization, forms a system differing very little in density from that which it becomes in the solid state. However, the comparison of this latter density with the value of δ_1 determined by calculation, is only admissible here on neglecting the slight inequalities by which the aqueous solutions of sugar-candy deviate from the law of simple mixture; as also on leaving out of question the difference which existed between the temperatures of these solutions and that at which the density of the sugar in the crystallized state was determined experimentally.

44. I have related in my memoirs several experiments on mixed systems, the proportions of which were determined by volumes, and which appear to me likewise to be formed without apparent contraction or dilatation. They were of such a nature that the liquids composing them might be supposed not to enter into a chemical combination with one another, at least in the ordinary sense. There were, for example, various essential oils mixed together, or with fatty oils rendered colourless by long exposure to light. The constancy of the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$ always accompanied this presumed state of simple mixture. I regret however that I did not then verify this presumption by the direct observation of the densities. But fortunately I am able to draw from my observations already published a much more decisive example than those could have been.

We shall see presently that the solutions of tartaric acid in water deviate constantly, and in all proportions, from the law of a simple mixture. Having formed such a solution, in accu-

rately determined proportions, I introduced a certain quantity of an aqueous sulphuric acid, the quantity of acid in which was known, and I observed the rotatory power of the mixed system which resulted. I then calculated the total proportions of water and of anhydrous sulphuric acid present; after which I formed another system of these two bodies only, in which they were associated in the same proportion, and I employed it to dilute progressively the first mixed system, by quantities the weights of which were determined. Now, whether it be from a special consequence of the relations thus established between the three elements of these systems, or by a more general property resulting from the constancy of the relation which is maintained between the sulphuric acid and the water, the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$ presented in all the same value, within very small fractions, for which I cannot answer. And (which I did not then remark) the densities of the successive systems are likewise derived from one another, conformably to the law of simple mixture, as I am about to prove.

This is an application of the equation (2.) of § 39, taken in its most general form. If we call δ_1 the density of the primitive tartaro-sulphuric system, ε_1 its proportion in each of the systems deduced from it, and δ_2 the density of the constant system σ, composed of anhydrous sulphuric acid and water, by the addition of which the successive dilutions are effected, the density δ of each mixed system thus formed will be, in the hypothesis of a simple mixture, determined by the following formula,

$$\frac{1}{\delta} = \frac{\varepsilon_1}{\delta_1} + \frac{(1-\varepsilon_1)}{\delta_2}. \qquad \ldots \quad (2.)$$

Not having then had this application in view, I did not think of measuring the density δ_2 of the system σ; but it may be determined from the quantities, the proportions of which I have given in my memoir (*Académie des Sciences*, tome xvi. p. 287), by applying to it the tables of densities given in the *Traité de Chimie* of M. Berzelius, the accuracy of which I had occasion to confirm for mixtures of water and sulphuric acid varying little from that in proportion. I thus found

$$\delta_2 = 1{\cdot}2015,$$

a result which every one can verify.

Now, according to the quantities of the mixture σ progres-

sively added which I have given in the place above cited of my memoir, I calculated the successive values of ε_1 for the different systems formed; and by adding to it the observed density δ_1 of the primitive system, I determined by the equation (2.) the resulting density δ, which I compared with the densities actually measured. The elements of these comparisons are seen in the following table, constructed on the model of those which I have already given.

Name of the observed system.	Ponderable proportion of the primitive system ε. ε_1.	Centigrade temperature at which the density δ was observed.	Density observed, that of distilled water being 1.	Density calculated by the formula (2.), on the hypothesis of a simple mixture. δ.	Excess of the observed density over the calculated density.
Primitive tartro-sulphuric system Σ_1	1·000000	13°·5	1·25895		
System Σ_2 deduced from Σ_1 by addition of σ	0·802047	13·0	1·24843	1·24715	+0·00128
System Σ_3 deduced from Σ_2 by addition of σ	0·608232	13·0	1·23703	1·23580	+0·00123

The differences expressed in the last column of the table are so slight, that they could not be relied upon in experiments which had not been performed with a view to such an application; and they may undoubtedly be neglected, especially on recollecting that the value of δ_2, which is an element of the calculation, has been determined from tables which were not perhaps exactly established for the same temperature. Thus, in this delicate state of equilibrium, in which the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$ appeared nearly constant, the chemical groups formed in the first system Σ_1 are diffused in the two others by simple dilution, without any reaction being exerted between them and the quantities of the mixture σ subsequently added.

45. But here are the proofs of the fact, which show that the converse of this proposition is not true, as I have stated above; that is to say, that in the present, as in many other cases of combinations, the chemical groups may experience very considerable modifications, which alter the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$ not only in its absolute values, but in its sign,

without any appreciable contraction or dilatation occurring among the liquid systems, whose mixture determines such great reactions.

This is seen by the numbers given at page 379 of the memoir cited, in the table mentioned above in No. 13*. They relate to a certain combination of tartaric acid, alumina and water, which, by simple additions of this liquid, passed progressively from left-handed to right-handed rotation, with a progressively increasing energy, and afterwards resumed its left-handed power by the abstraction of water. Now, in all these considerable changes of chemical constitution, the primitive system is associated with water as in the case of a simple mixture, without appreciable contraction or dilatation.

This is another application of the equation (2.), § 39, in which we must make $\delta_2 = 1$, since the inactive liquid progressively added is pure distilled water. Thus, calling ε_1 the ponderable proportion of the primitive system which enters, with the density δ_1, into each of those deduced from it, the resulting density δ calculated on the supposition of a simple mixture will be, as in § 42,

$$\delta = \frac{\delta_1}{\varepsilon_1 + (1 - \varepsilon_1)\,\delta_1}; \quad \ldots\ldots \quad (2.)$$

the value of δ_1 is given in the table cited, and that of ε_1 is also mentioned there for each of the successive systems. We have then all the necessary elements for calculating the resulting densities δ, which I compare with those which have been really observed. Such is the object of the following table.

* I avail myself of the opportunity here offered to rectify a typographical error in column 9 of the table cited. It is entitled actual *specific* rotatory power of the liquid for 100mm, and $\frac{\alpha}{l\delta}$ is added as the sign of this power: but it should be $\frac{\alpha}{l\varepsilon\delta}$; for the numbers which the column contains are calculated according to this expression. I must add moreover that they apply to observations made with the naked eye, without the intervention of red glass. The last number, — 18·992, is the only one which corresponds to the quantity $\frac{\alpha}{l\delta}$; and it was requisite, in fact, to calculate it thus, because the liquid observed being the product of a concentration of all the united residues of the preceding ones, the quantities were unknown.

Name of the observed system.	Ponderable proportion in the primitive system A. t_1.	Centigrade temperature at which the density was observed.	Density observed, that of distilled water being 1.	Density calculated by the formula (2.) on the hypothesis of a simple mixture. s_1.	Excess of observed density over the calculated density.	Direction of the deviation produced on polarized light.
Primitive tartro-aluminic system A.....	1·00000	+14°	1·14771	.....	.....	very considerable.
B deduced from A by addition of water	0·50261	+14	1·06990	1·06916	+0·00074	feeble.
C deduced from B by addition of water	0·25195	+15	1·03467	1·03351	+0·00116	increasing.
D deduced from C by addition of water	0·13064	+13	1·01803	1·01710	+0·00093	increasing.

NOTE.—We have not comprised in these comparisons the system E mentioned in the printed table, and the dilution of which was still greater, because we had accidentally omitted to observe its density. But as it should differ very little from the unit, we were contented to derive it from D by the hypothesis of a simple mixture. The temperatures of the weighings given in the third column are those which I have found in my note-book.

The differences between the densities observed and those deduced from the hypothesis of a simple mixture are here too small to be relied upon; and we must conclude that, within the limits of precision which my processes for obtaining the specific gravity allowed, these systems which experienced such considerable molecular changes that the direction of their rotation changed and always increased specifically, are nevertheless derived from one another by addition of water, with no changes of volumes, or excessively slight ones.

46. I now come to the aqueous solutions of tartaric acid. For these, if we compare their densities for various proportions, and at one and the same temperature, it is found that they are connected with one another by a hyperbolic law, the precision of which is such that it may be substituted for the quantities by weight without any errors resulting which could be noticed in the usual processes of taking the densities. I have established this fact in a memoir inserted among those of the Institute, t. xv. pp. 124 *et seq.* Since I have been aware of the fact, I have made numerous applications of it, which have all confirmed its truth. I shall admit it therefore in what follows. The following is the statement which I then gave. Let y be the proportion

of acid, in the unity of weight, expressed in hundredths; x the excess of the resulting density above unity, expressed in thousandths, this density being taken comparatively to that of distilled water at the same temperature. The relation of x to y is

$$x = \frac{ay}{y - b};$$

a and b are two constants which, at the temperature of 6°·8 C., have the following numerical values:—

$$a = -1380{\cdot}875, \qquad b = +302{\cdot}7003;$$

both these values increase, preserving their proper sign, in proportion as the temperature rises.

To reduce this statement to the notations which we have adopted in the course of the present memoir, let δ be the absolute density of the system, that of water being 1, and ε the proportion by weight of acid existing in each unit of weight of the solution. According to the definitions above given of x and of y, we evidently have

$$x = 1000\,(\delta - 1), \qquad y = 100\,\varepsilon;$$

introducing then these expressions instead of x and y into the preceding algebraic relation, we shall derive from it

$$\delta = 1 + \frac{\frac{1}{10}\,a\,\varepsilon}{100\,\varepsilon - b}.$$

Thus, making, for the sake of abbreviation,

$$a' = \tfrac{1}{10}\,a = -138{\cdot}0875, \qquad b = +302{\cdot}7003,$$

we have, at the temperature of 6°·8, which I take for example,

$$\delta = 1 + \frac{a'\,\varepsilon}{100\,\varepsilon - b};$$

as this law is maintained without discontinuity in all the proportions in which the solutions may be observed in the liquid state, we may extend it even to the case where the proportion of water is null, which would suppose $\varepsilon = 1$. Then the resulting density, which I shall call δ_1, would be that of the acid uncrystallized alone, in the molecular state of disaggregation. We should thus have

$$\delta_1 = 1 + \frac{a'}{100 - b}.$$

By giving to the constants a' and b their proper numerical va-

lues at the temperature of 6°·8, I found in the memoir cited that the density δ_1, thus calculated for the state of disaggregation, is lower than that of the solid crystallized acid only in the relation of 57 to 59.

Whatever it may be, as it is one of the terms of the hyperbolic law, it may be taken numerically as a starting-point, and all the other densities derived from it according to the corresponding values of ε. With this view I take the expression of the constant a' in function of δ_1 by the preceding relation, and substitute it in the general expression of the density δ, which I shall henceforth call δ_h, in order to call to mind that it is calculated in the hyperbolic law. I thus find

$$\delta_h = \delta_1 + \frac{b\,(1-\varepsilon)\,(\delta_1 - 1)}{100\,\varepsilon - b}. \quad . \quad . \quad . \quad . \quad (a.)$$

Now, I take the expression of the density δ by deducing it from δ_1 by the law of simple mixtures, and represent it by δ_m, in order to distinguish it from the preceding. The equation (2.) of § 39 being applied to this case, with $\delta_2 = 1$ gives, as we have already seen in § 42,

$$\delta_m = \frac{\delta_1}{\varepsilon + (1-\varepsilon)\,\delta_1};$$

thence we easily derive

$$\delta_m = \delta_1 - \frac{(1-\varepsilon)\,\delta_1\,(\delta_1 - 1)}{\varepsilon + (1-\varepsilon)\,\delta_1}. \quad . \quad . \quad . \quad . \quad (b.)$$

On subtracting this expression from that of δ_h, the result is

$$\delta_h - \delta_m = (1-\varepsilon)\,(\delta_1 - 1)\left\{\frac{b}{100\,\varepsilon - b} + \frac{\delta_1}{\varepsilon + (1-\varepsilon)\,\delta_1}\right\},$$

and on reducing to a common denominator the factor included within the parentheses,

$$\delta_h - \delta_m = \frac{(1-\varepsilon)\,\varepsilon\,(\delta_1 - 1)\,[b + (100-b)\,\delta_1]}{(100\,\varepsilon - b)\,[\varepsilon + (1-\varepsilon)\,\delta_1]}.$$

Now, the equation which determines δ_1 gives

$$(100 - b)\,\delta_1 = 100 - b + a',$$

whence

$$b + (100 - b)\,\delta_1 = 100 + a';$$

consequently

$$\delta_h - \delta_m = \frac{(1-\varepsilon)\,\varepsilon\,(\delta_1 - 1)\,[100 + a']}{(100\,\varepsilon - b)\,[\varepsilon + (1-\varepsilon)\,\delta_1]}. \quad . \quad . \quad (c.)$$

From the nature of the physical problem, the ponderable pro-

portion of acid ε is always a fraction less than unity, which renders the product $(1-\varepsilon)\,\varepsilon$ positive; $\delta_1 - 1$ is also positive, since the density of the disaggregated acid surpasses that of the water. The relation

$$\frac{(1-\varepsilon)\,\varepsilon\,(\delta_1 - 1)}{\varepsilon + (1-\varepsilon)\,\delta_1}$$

is therefore essentially positive by these conditions. But, at the temperature of 6°·8, which we are considering, the values of a' and of b are such, that we have

$$100 + a' = -38{\cdot}0875, \quad 100\,\varepsilon - b = -302{\cdot}703 + 100\,\varepsilon.$$

These two factors are therefore both negative, and they remain so at all observable temperatures, which renders their ratio positive. Hence, under all the circumstances which the experiment may present, the difference $\delta_h - \delta_m$ is always positive; that is to say, that, generally, the real density δ_h, observed or calculated by the hyperbolic law, exceeds the density δ_m calculated hypothetically by the law of simple mixture. These densities occasionally become equal only in the two extreme cases in which we should suppose $\varepsilon = 1$ or $\varepsilon = 0$. In fact, when $\varepsilon = 1$, the system is entirely formed of disaggregated acid whose density is δ_1, a circumstance which we have taken as the common starting-point in the general expressions of δ_h and of δ_m. The other case, in which we take $\varepsilon = 0$, supposes that the solution under consideration contains no acid, or only an infinitely small quantity in comparison to the quantity of distilled water associated with it. Then δ_h and δ_m should still be equal, as becoming both the one and the other equal to unit; and it is also to this common value that their individual expressions are reduced, as may easily be verified.

47. Between these two extremes the difference $\delta_h - \delta_m$ attains a maximum of value corresponding to that of the variable factor

$$\frac{(1-\varepsilon)\,\varepsilon}{(100\,\varepsilon - b)\,[\varepsilon + (1-\varepsilon)\,\delta_1]};$$

in order to determine simply its conditions, I substitute for ε a new variable n, so that we have

$$(1-\varepsilon) = n\,\varepsilon,$$

consequently

$$\varepsilon = \frac{1}{n+1};$$

n evidently represents the multiple of water associated with the acid. Thus its value should always be positive like those of $1 - \varepsilon$ and of ε. Eliminating therefore the latter by its expression in n, the function considered becomes

$$\frac{n}{[100 - b(n+1)]\,[1 + n\delta_1]};$$

or, on developing the denominator,

$$\frac{n}{100 - b + [(100 - b)\delta_1 - b]\,n - b\delta_1 n^2}.$$

On differentiating it in this form, relatively to n, we find, as the condition of its maximum,

$$0 = 100 - b + b\delta_1 n^2,$$

whence

$$n = +\sqrt{\frac{b - 100}{b\delta_1}};$$

and as, by the hyperbolic relation, we have

$$\delta_1 = 1 + \frac{a'}{100 - b},$$

there finally results,

$$n = +\frac{b - 100}{\sqrt{b\,[b - 100 - a']}};$$

an expression which contains only the constants of the hyperbolic relation proper to each temperature.

For the temperature of 6°·8 I found, at page 134 of my memoir,

$$a' = \tfrac{1}{10}\,a = -138{\cdot}0875,\quad b = +302{\cdot}7003;$$

these numbers give

$$n = 0{\cdot}63111,$$

consequently

$$\varepsilon = \frac{1}{n+1} = 0{\cdot}61318.$$

The value of ε exceeds a little that at which the solution might remain liquid at the temperature under consideration, for, at the temperature of 8°, I found as the limit of the liquidity $\varepsilon = 0{\cdot}548134$, as will be seen at page 139 of my memoir. Thus, in all the physical phases, in which such a system may preserve the permanent state of liquidity, the action of the acid to contract the water added to it, decreases in proportion as the relative quan-

tity of the latter increases. But the effect of this action does not become mathematically null until the total proportion of the water is infinite compared with that of the acid contained in the solution.

I proceed now to prove that the values of the characteristic function $\frac{\alpha(P+E)}{Pl\delta}$, determined by the optical experiments, follow precisely laws of variation analogous to these, in similar solutions; so that they likewise agree in showing that *tartaric acid dissolved imparts a power to the whole mass of water present, which is not completely satisfied until the proportion of this liquid becomes comparatively infinite.* Such is the principal object of the following section.

SECTION III.—*On the action of tartaric acid upon water and other bodies exposed to it in the liquid state.*

48. I consider an aqueous solution of tartaric acid in which P represents the weight of the acid, E that of the water associated with it. To render its definition independent of the units of weight of P and E, I make

$$\varepsilon = \frac{P}{P+E}, \qquad e = \frac{E}{P+E},$$

whence

$$\varepsilon + e = 1;$$

ε will be the proportion of acid, e the proportion of water contained in each unit of weight of the solution. I make, moreover, for the sake of shortness,

$$[\alpha] = \frac{\alpha(P+E)}{Pl\delta} = \frac{\alpha}{P\varepsilon\delta},$$

α designating the deviation observed through a red glass, which only allows red rays sensibly homogeneous to pass. $[\alpha]$ will be the characteristic function, determinable by observation, of which we have given, in § 27, the relations with the various possible states of the active chemical groups constituting the system under consideration. Now, in the investigation contained in vol. xv. of the *Mémoires de l'Académie des Sciences*, I have established, by numerous experiments, the fact, that if we form a series of similar systems, in which ε and e vary in every degree compatible with the state of liquidity, and that we observe the action of all these systems on polarized light, *at the same temperature,*

the values of $[\alpha]$ present a continuous and regular course of variation, which is expressed with all the precision of the observations themselves, by a rectilinear function of the form

$$[\alpha] = (A) + (B)\, e,$$

(A) and (B) being two numerical coefficients independent of e and ε. The coefficient (A) varies regularly with the temperature; it increases in proportion as that rises, and decreases when it falls. Its value becomes null toward the temperature of 23° C., and it remains positive above that limit, negative below it. The coefficient (B), on the contrary, appeared independent of the temperature; and on evaluing $[\alpha]$ for a thickness of 100 millimetres, I found it equal to 14°·3154, relatively to the red ray. The collection of experiments, from which these determinations have been deduced, embraces the interval of temperature comprised between −5° and +26°. After having described them in detail in the memoir cited above, I resumed them in a subsequent investigation, inserted in vol. xvi. of the *Mémoires de l'Académie*, where they have been confirmed by new applications. Although the rectilinear law of the variations of $[\alpha]$ could not be proved directly except for the red ray, I have shown, by various proofs, that it should be extended to the other simple rays, with different values of the coefficients (A) and (B); whence results the speciality of tints which these solutions produce in the images formed by the analysing prism, when the polarized beam passed through it is composed of white light.

49. From what has been established in the first section, § 27, the function designated here by $[\alpha]$ is that whose variability or constancy characterizes the state of combination, or of non-combination, of the active substance with the inactive liquid into which it has been introduced. Since it is here variable for the different proportions of water in which the acid is dissolved, it is a certain proof that it is combined, and not in the state of simple mixture. This consequence is, in fact, confirmed by the mode of variation of the densities of tartaric solutions formed successively with various proportions of water, as we have seen in § 46. According to § 27, already cited, the several systems of simple or complex combinations, which may most probably be effected in similar cases between the two bodies present, give rise to certain forms of variability of the function $[\alpha]$ which we have there defined. It thus becomes necessary to establish with precision, in all its details, that which it assumes in the

actual case, in order to ascertain to which of those forms it should be referred, and to deduce from it the system of combination produced.

50. I have not been able to preserve, without precipitation, the tartaric solutions in the combined conditions of a sufficiently low temperature, with a sufficiently small proportion of water, to observe directly the rotatory power $[\alpha]$ becoming negative by the predominance of the coefficient (A) over the term (B) e. But, guided by the preceding indications, I produced an analogous effect, by introducing into these solutions sulphuric acid, which, from its affinity for water, rendered it less free, without opposing an absolute obstacle to the state of liquidity. For, in an experiment made thus at the temperature of + 14° C., I succeeded in rendering the deviation of the red rays towards the right almost null, and in making that of the violet rays pass to the left; so that I cannot doubt that the deviations of all the rays, in such a system, would have become in like manner negative if they had been observed at lower temperatures. I obtained this complete inversion by adding to the tartaric solutions large proportions of solutions of potass, and also by dissolving in very small quantities of water tartrates of alumina properly prepared. But although the tendency of the tartaric acid to invert its power, when deprived of water, or when this is withdrawn from its affinity, is evident in these last phænomena, it is complicated by the union which it contracts with the other bodies placed in its presence, so that the even partial inversion effected by the presence of sulphuric acid affords a better demonstration.

51. From the mean and constant value + 14·3154 which the coefficient (B) is found to possess in the purely aqueous solutions of tartaric acid, the right line represented by $[\alpha]$ forms with the axis of the abscissæ e an angle of 86° 0′ 15″, so that it is almost perpendicular to it. For this reason, in fig. 1, Plate V., where we have represented it for a temperature at which the coefficient (A) would be negative, it was necessary to trace it under an imaginary inclination far less than the real one, in order to distinguish it sensibly from the axis of the $[\alpha]$. This alteration is without inconvenience in a purely conventional graphic representation, since it amounts to the constructing the e and the $[\alpha]$ on a different scale of lengths; but the circumstance which renders it necessary, points out a physical peculiarity which it is very essential to examine. At the mean temperatures

at which these experiments are usually made, it is scarcely possible to obtain stable tartaric solutions, that is to say which remain in the liquid state when proportions of water e are employed less than 0·4; neither can we suppose e to have become, by dilution, greater than 1, since at this last limit the corresponding proportion $1 - e$ of acid would necessarily be null or infinitely small, so that we could perceive the deviations only through tubes of an infinite length. For this reason it is requisite to restrict the dilution to values of e considerably less than 1, in order to avoid very long tubes. But, fortunately, towards this second limit of e, the values of $[\alpha]$ experience only such slight changes, that they evidently tend towards a constant and not distant limit. I thus made the observations up to $\epsilon = 0{\cdot}95$, and always observed the rectilinear form of $[\alpha]$ maintained. Now, when physical phænomena present laws of simple proportionality, relatively to the values of one of their elements, of which the observable phases of variation are comprised within such narrow limits, it may always be suspected that this proportionality expresses only the first term of the development of the complete laws; so that the straight line representing it is really nothing more than the initial tangent of the curve which expresses these laws. But although both modes of construction are then equivalent for the numerical representation of the observed results, they are far from being so as regards the determination of the physical analogies which it is so important to establish among the phænomena in which they exist. For the simple proportionality which suffices as an approximation for some of them, would evidently render these analogies misunderstood if it were supposed rigorous.

52. The necessity of applying these considerations to the tartaric solutions appeared manifest, when, in a subsequent investigation, I followed the varied properties which they present in their combinations with other bodies, particularly with boracic acid; and I then indicated the curvilinear law which it seemed to me should be substituted for the law of simple proportionality. (*Mém. de l'Académie*, vol. xvi. p. 259.) I proceed to establish here this generalization.

It consists in replacing the rectilinear law of the $[\alpha]$ by a hyperbolic law, expressed under the following form,

$$[\alpha] = A + \frac{B\,e}{e + C},$$

A, B, C being three constant coefficients for all the observations made at the same temperature, whatever be the proportion of water designated by e. The geometrical locus of e and $[\alpha]$ then becomes an equilateral hyperbola, having its asymptotes respectively parallel to the axes of the rectangular coordinates of e, $[\alpha]$, and the general disposition of which is represented in fig. 2, for the case in which the coefficient A is negative, in order to assimilate it to the analogous case which we have supposed in the construction of the rectilinear locus. The centre C of this hyperbola is situated at the point whose algebraic abscissa O X would be $e = -C$, and the ordinate C X, $[\alpha] = A+B$. Its summit S corresponds to the abscissa O H, in which $e = -C + \sqrt{BC}$: and it has for its ordinate H S, where $[\alpha] = A+B-\sqrt{BC}$. The point D, taken on the curve, for the abscissa $e = 0$, answers to the case in which the system contains no water associated with the acid, which gives $[\alpha] = A$; and it has been constructed, like the right line of fig. 1, for the case in which the coefficient A is negative. It is therefore on starting from this point D that the hyperbolic relation commences at most to be realized by experiment, and only for positive values of e. Again, its *physical* application does not extend indefinitely to all these values, because, from the nature of the problem, e representing the proportion by weight of the water associated with the acid, it should always remain less than unit, which is its extreme limit. The ordinate $[\alpha] = A + \frac{B}{1+C}$, which corresponds to the abscissa $e = 1$, expresses therefore the greatest *physical* value which $[\alpha]$ can attain; and as the coefficient C has always a positive numerical value sufficiently considerable, as we shall presently see, this extreme $[\alpha]$ is always much less than the asymptotic ordinate $[\alpha] = A + B$, and even than the ordinate of the summit S, $[\alpha] = A+B-\sqrt{BC}$. So that the hyperbola can only be realized in a very small portion of its geometric course, from the point D to a point far below the summit S; and for this reason it can scarcely be distinguished from a straight line in this limited arc.

I shall explain at the end of this memoir the process of calculation most convenient in order to adapt this hyperbolic law to observations, and to deduce thence the numerical values of the coefficients A, B, C. In the present case, in order not to inter-

rupt the course of reasoning, I shall suppose this determination effected, and shall content myself with relating the evaluations which result in the cases employed as examples.

53. But before passing to these particular applications, it is desirable to examine, by analytical considerations, under what conditions such a hyperbola can be substituted, as an expression of the experiments, for the rectilinear form which reproduces them so approximately; that is to say, we must characterize generally the relations of magnitude and of sign which the values of the coefficients A, B, C ought to have amongst them in order to produce the expected equivalence. For if these considerations are realized, when adapted to the observations, the equivalence in question will become more surely admissible than if it could be attributed to an accident of numbers.

In the first place, if we apply the hyperbola to temperatures low enough for the coefficient (A) of the right line to be negative, the coefficient A must present itself also with the same sign as (A), and, moreover, with an equal or slightly different value; for the two laws coincide analytically when e is null, so that they should give identically, for this case, the same value of $[\alpha]$ if the observations were absolutely exact. Consequently, the two coefficients A and (A) ought not to differ from one another, as regards sign and value, except within the limits of error of the results employed for their determination, owing to the different manner in which these results enter into them.

Secondly, I assert that the coefficient C should be a number large enough, and such as that the relation $\frac{B}{C}$ differs very little from the primitive coefficient (B), both as to its sign and absolute value. For if this condition is fulfilled, since e is always a fraction less than 1 in the physical applications, the factor $\frac{B}{e+C}$, although analytically variable, will always have values nearly constant in the particular cases of experiment to which it is applied; which, joined to the essentially fractional character of e, will always give a product $\frac{Be}{e+C}$ very nearly proportional, or even sensibly proportional to e, as the rectilinear approximation presented it.

54. Now, to show with what accuracy all these considerations

are realized, I select a series of fifteen experiments published in vol. xv. of the *Mémoires de l'Académie*, page 208; it comprises the observations of as many different tartaric solutions, in which the ponderable proportions of water varied from $e=0{\cdot}40399$ to $e=0{\cdot}95083$. The mean temperature at which all these solutions were observed was + 12°·68, with slight variations near this value, as may be seen at page 205, where the temperature of each observation is given. All the values thus obtained for $[\alpha]$ were connected by the rectilinear form

$$[\alpha] = (A) + (B)\, e,$$

and, on determining the coefficients (A), (B), by the condition of satisfying the two extreme observations alone, I found

$$(A) = 1{\cdot}17987; \qquad (B) = + 14{\cdot}3154;$$

which consequently gives for any value of e,

$$[\alpha] = - 1{\cdot}17987 + 14{\cdot}3154.\ e.$$

Then, on calculating the values of $[\alpha]$ by this formula, according to the value of e proper to each experiment, and comparing them with the observed values, the agreement was such, that I could not answer for the small differences which occasionally occurred, as may be seen at page 208 already cited.

55. At present, to submit these same results to the hyperbolic relation, I first take the two same extreme data; and, as it is necessary to add a third, since we have three coefficients to determine, I chose for this purpose a mean between the simultaneously observed values of $[\alpha]$ and of e, which corresponded to the mean of the entire series, which had not entered into the primitive calculation of the coefficients (A), (B) of the rectilinear relation. Operating thus, I found

$$A = - 1{\cdot}55526; \quad B = + 226{\cdot}3727; \quad C = + 14{\cdot}4455;$$

and consequently

$$\frac{B}{C} = + 15{\cdot}67075; \qquad \frac{1}{C} = 0{\cdot}069225;$$

whence is generally deduced

$$[\alpha] = - 1{\cdot}55526 + \frac{226{\cdot}3727\ e}{e + 14{\cdot}44555};$$

or again,

$$[\alpha] = - 1{\cdot}55526 + \frac{15{\cdot}67075\ e}{1 + e.\,0{\cdot}069225}.$$

All the relations which we had foreseen between the numerical coefficients A, B, C, are here very precisely realized, both as regards their signs and their relative magnitudes. For, first, the excess of A over (A) is only 0·37539: then, $[\alpha]$ being here expressed in degrees in the two laws, there would only result a difference of $22' 31''$ over its evaluation in degrees, for the case of e null, if that case could be realized experimentally; and this deduction, which is the furthest removed from the determining data, could only be obtained within this limit of certainty by reiterated observations. The other extreme evaluation of $[\alpha]$ corresponding to $e = 1$, presents a still nearer agreement, as less distant from these same data; for it is found to be $+ 13°·1355$ by the rectilinear law, and $+13°·10024$ by the hyperbola, which does not present any difference physically appreciable. The coincidence of the intermediate values of $[\alpha]$ is rendered evident if their hyperbolic expression be considered in its second form. For, in truth, the coefficient of e, $15°·67075$, there exceeds a little its analogue of the rectilinear relation, which is only $14°·3154$. But this latter is only divided by unity in the rectilinear expression of $[\alpha]$, whilst the corresponding term of the hyperbola is divided by $1 + e \,.\, 0·069225$, a number always somewhat greater than 1; and it is this that produces the exact agreement of the two values of $[\alpha]$ at their extreme limit, where $e = 1$. We may therefore legitimately consider these two general expressions of the phænomenon as being equally admissible, and numerically equivalent within the limits of uncertainty which the observations admit; but the hyperbolic law is physically preferable, because it is less restricted. And if other phænomena of combination, analogous to those, but more extended or more energetic, reproduce it with undoubted curvilinear characters, as in fact we shall see further on, there will be the strongest presumption that it is this which is actually realized, although in a less evident manner, in the successive but less intimate combinations of tartaric acid with water.

56. Having thus demonstrated these two equivalent modes of variation of the function $[\alpha]$ which our experiments realize, let us compare them with the various forms which that function may assume in the systems composed of an active substance and an inactive liquid, forms which we have enumerated and characterized in § 27 for all the supposable physical states of similar

systems. In the first place, the mere fact of the continuous variation of $[\alpha]$ for any values whatever of e, that is to say for any proportions of water, shows us that, whatever be the amount of this liquid, the acid is never completely saturated or supersaturated with it, so as to form with it fixed groups which a subsequent addition of water would not further modify. We have noticed this in § 46, in discussing the mode of variation of the densities offered by mixed systems thus constituted. Considering therefore the state of non-saturation doubly manifested by these experiments, I assert that the mode of variation of the function $[\alpha]$, here realized by the experiment, excludes the supposition of the division of the active substance into two portions, one of which is completely saturated and the other free. For, in this case, the second of those which we have enumerated in § 27 as belonging to the general phase of non-saturation, we have established that the function $[\alpha]$ should vary as the ordinate of a right line, of which the relation $\frac{E}{P}$ would be the abscissa. Now, such a mode of variability is incompatible with the actual mode of variation which we have proved by observation.

57. To demonstrate this fact, it will suffice to employ the simplest of the equivalent expressions which we have obtained of $[\alpha]$, that is to say the rectilinear, the hyperbolic leading exactly to the same conclusion, as may be easily proved. Taking, therefore, the simple expression

$$[\alpha] = (A) + (B)\, e,$$

it is seen that the abscissa of the real right angle is e, or $\frac{E}{P+E}$, instead of $\frac{E}{P}$, a very different result. To show the incompatibility of these two forms under the conditions of exactitude required by the experiments, let us make

$$\frac{E}{P} = x, \text{ whence } E = P\,x,$$

we thence deduce

$$e = \frac{E}{P+E} = \frac{x}{x+1}, \qquad e = \frac{P}{P+E} = \frac{1}{x+1};$$

then, substituting this expression of e in the rectilinear ex-

pression of $[\alpha]$, which is given by experiment, there will result

$$[\alpha] = (A) + \frac{(B)\,x}{x+1},$$

whence we shall have

$$(A) = -1{\cdot}17987; \qquad (B) = +14{\cdot}3154.$$

Now, if we take x or $\frac{E}{P}$ as the abscissa, $[\alpha]$ will be the ordinate, not of a right line, but of an equilateral hyperbola, having its asymptotes parallel to the axes of the rectangular co-ordinates of $[\alpha]$ and x, as represented in fig. 3, where the letter O designates the common origin of these co-ordinates. The centre C of this hyperbola is placed at the point whose abscissa O X is $x = -1$, and the ordinate C X, $[\alpha] = (A) + (B)$. Its summit S, consequently its most curved portion, corresponds to the abscissa O H, whose value is $x = -1 + \sqrt{(B)}$, which gives, for the ordinate H S, $[\alpha] = (A) + (B) - \sqrt{(B)}$. We have therefore at this summit, $x + 1 = \sqrt{(B)}$, consequently $\varepsilon = \frac{1}{\sqrt{(B)}}$, which determines the ponderable proportion of acid answering to it, which being only a function of the single coefficient (B), is, like it, independent of the temperature. By substituting for (B) the number 14·3154, which is its value in the rectilinear expression of $[\alpha]$, calculated for 100 millimetres, we deduce $\varepsilon = 0{\cdot}2643$, a value proveable by experiment. For this reason, having adopted this length to express $[\alpha]$ relative to the red ray which I have taken as type, I multiplied the experiments between the values of ε, 0·20 and 0·34, in order to confirm the curvature of the hyperbola with full certainty. In fact, the values of $[\alpha]$ obtained in this interval being constructed graphically, manifest this curve in so decided a manner, that it is impossible to mistake it. And the course of the numerical values of $[\alpha]$ moreover proves this result with greater strictness; for, agreeing with the rectilinear relation, of which e or $\frac{E}{P+E}$ is the abscissa, with an accuracy equal to that of the observations themselves, they are consequently incompatible with a similar relation, in which the abscissa is $\frac{E}{P}$. The uninterrupted continuity of their variations, conformably to the rectilinear or hyperbolic law, of which the

abscissa is e or $\frac{E}{P+E}$, does not render them less incompatible with the more complex supposition which would transfer them successively, by abrupt intermittences, to different right lines having for abscissæ $\frac{E}{P}$, as in the third possible case of the phase of non-saturation, which we have discussed in § 27.

58. Since, therefore, among the three mechanically supposable modes of constitution of non-saturated solutions which we have established, there are two which we find incompatible with the law of variation assigned to the function $[\alpha]$ by experiment, in so far as they suppose that the whole mass of acid, or a portion of this mass, forms with water fixed groups, which a subsequent addition of this liquid does no further modify, it is requisite, excluding these, to admit the third, which consists in the fact, that the acid forms, with the water presented to it, groups perpetually variable, which only become fixed by an infinite addition of water. Now, this is precisely the same consequence to which we were led in discussing the physical law, according to which the densities of the solutions here considered are modified, without term or limit, by fresh quantities of water subsequently added.

59. Thus, from these two independent classes of facts, it equally results that, in liquid systems composed of tartaric acid and water in different quantities, at a constant temperature, the water does not combine specially with certain molecules of the acid, forming with them complete and saturated chemical groups, but is divided among them all uniformly, so as to form groups always incomplete, which become the actual constituent elements of the total mass. The specific deviating action of these groups is therefore expressed in each solution by the function $\frac{\alpha}{l\delta}$, proper to media of uniform constitution, as we have seen in the first case of non-saturation in § 27, which is here realized. Now, the physical and rectilinear law

$$[\alpha] = (A) + (B)\,e,$$

which represents the variations of the function $[\alpha]$, allows us to calculate generally those of the function $\frac{\alpha}{l\delta}$. In fact, since we have

$$[\alpha] = \frac{\alpha}{l\varepsilon\delta} \text{ and } \varepsilon + e = 1,$$

there results

$$[\alpha] = \frac{\alpha}{l\delta(1-e)};$$

substituting then this expression of $[\alpha]$ in the first member of our rectilinear equation, and deducing the relation $\frac{\alpha}{l\delta}$, we have

$$\frac{\alpha}{l\delta} = (\mathrm{A}) + [(\mathrm{B}) - (\mathrm{A})]\,e - (\mathrm{B})\,e^2,$$

a relation in which e represents the proportion of water associated with the acid, as previously. When $e = 0$, the second member is reduced to (A), that is to say to the proper power of the acid, without addition of water, at the temperature at which the experiment is made. When $e = 1$, it becomes null, because the solution is only pure water. It becomes null again when e is equal to $-\frac{(\mathrm{A})}{(\mathrm{B})}$; but this second value is only physically realizable at temperatures lower than 23°, at which (A) is negative; because if (A) were positive, it would suppose that water were removed from the acid instead of being added to it. Between these extreme limits of e, the values of $\frac{\alpha}{l\delta}$ are the ordinates of a parabola of the second degree, of which e is the abscissa, and which is represented in fig. 4, in the supposition of (A) being positive. The axis S H of this parabola is parallel to the right line O Y, on which the ordinates $\frac{\alpha}{l\delta}$ are measured from the origin O; and it is distant from this right line by a quantity O H equal to $\frac{(\mathrm{B}) - (\mathrm{A})}{2\,(\mathrm{B})}$. The proportion of water e equal to this value is therefore that which, for each temperature, gives to the groups of water and acid the most energetic rotatory power, whose expression is $\frac{[(\mathrm{A}) + (\mathrm{B})]^2}{4\,(\mathrm{B})}$. But it is easy to perceive that this relation does not correspond to a constant number of chemical equivalents supposed invariable. For the proportion of water which it gives being $\frac{(\mathrm{B}) - (\mathrm{A})}{2\,(\mathrm{B})}$, the corresponding proportion of acid is $\frac{(\mathrm{B}) + (\mathrm{A})}{2\,(\mathrm{B})}$; and $\frac{(\mathrm{B}) - (\mathrm{A})}{(\mathrm{B}) + (\mathrm{A})}$ is the relation by

weight between the water and acid. Now, the two terms of this relation include the coefficient (A), which varies with the temperature, whilst (B) does not vary sensibly, at least in the interval of temperatures which my experiments have comprised. It is therefore evident that the relation itself changes in value when the temperature changes, so that the maximum of rotatory power of the groups corresponds to proportions always varying of the two combined principles. Nevertheless, the form of the parabola remains invariable for the same luminous ray, at every temperature, since its parameter depends only on (B). The influence of the intervention of water on the maximum of molecular power is readily perceived in the expression of the relation of the ponderable elements to which this maximum answers. It is only necessary for this purpose to give it the following form:—

$$\frac{(B) - (A)}{(B) + (A)} = 1 - \frac{2\,(A)}{(B) + (A)}.$$

Let us admit the constancy of (B) at all temperatures, as well as the variability of (A) as found by our experiments. Towards 23° C. (A) becomes null, and the maximum power of the molecular groups takes place for equal weights of water and acid. Above 23°, (A) being positive, the fraction annexed to the unit becomes negative: there is then less water than acid needed; and if A increased indefinitely, the maximum would correspond to an amount of water less in proportion as the temperature increases. As the ponderable relation of the two elements must be positive from the nature of the physical question, it would reach its least value, which is null, if (A) could become equal to (B), in which case no water should be added to the acid; and at still higher temperatures, every addition of water would weaken the action. Below 23°, (A) becoming negative, the circumstances would be reversed; the maximum of power would answer to a greater proportion of water than acid, and to an amount proportionately greater as (A) increases in this direction. Lastly, if its negative value could become equal to the constant and positive value of (B), the maximum power would only be obtained by the employment of an infinite portion of water.

60. I have thought it useful to develope these details, because by pointing out all the variations of the general action which the tartaric solutions exercise on polarized light, and deriving

them all from one and the same formula, which comprises the whole without ever failing, an agreement so extensive and so constant offers the most convincing proof of the accuracy of the indications which the optical characters furnish, and thus establishes the deductions drawn from them as to the molecular state of systems in which such characters may be observed. For the tartaric solutions in particular, it evidently results that *the acid, however weak in quantity, affects the whole mass of water presented to it*, since it produces in *the whole* of this mass a rotatory power which it did not itself possess; as we have already been led to conclude in discussing the course of the densities of solutions thus formed. Now, an influence so unlimited necessarily supposes the alternative of an action exercised immediately at a sensible distance, or communicated from particle to particle at every distance with a decreasing energy, in the same way as a natural magnet, or a bar of steel rendered magnetic, communicates its power to the soft and non-magnetic iron placed in contact with it. I leave to physicists to decide which of these two modes is the most probable.

In the memoir on some points of chemical mechanics which I have inserted in vol. xvi. of the collection of the Academy, I have described a great number of facts which lead to the same conclusion. They are founded on the complex reactions which are exercised in liquid systems, in which tartaric acid is associated with water and other bodies, alkaline or earthy, under the influence of their mutual affinities. I content myself with referring to them, and I proceed to add here some new proofs of the same kind which have been carried much further.

SECTION IV.—*On the reactions which take place in the ternary systems formed by tartaric acid, boracic acid and water, at a constant temperature.*

61. Many celebrated chemists have expressed very different opinions on the nature of the combinations which tartaric acid forms with boracic acid in the presence of water, and the existence, or at least the stability, of such a combination has even been called into doubt *.

Optical observations leave no uncertainty in this respect. They prove that systems composed of these three bodies may

* Thenard, *Traité de Chimie*, 6th edition, tome iv. p. 35; Dumas, *Traité de Chimie, appliquée aux Arts*, vol. v. p. 304.

exist, in proportions indefinitely varied, in the liquid state, forming chemical groups of variable constitution, according to the proportion of the elements of each system. We may even, in very general cases, discover by these means the numerical law according to which the constitution of the groups varies progressively with these proportions.

The existence and the character of these combinations are manifested immediately by the following experiment. If, to an aqueous solution of tartaric acid of a known quantity, a cold aqueous solution of boracic acid is added, in such proportions that the resulting system may exist in the liquid state, this system acts on polarized light quite otherwise than the primitive tartaric solution. Its specific action on one and the same simple ray is always more energetic; and it is exercised on luminous rays of various refrangibilities according to other laws of dispersion. The difference is manifested as soon as boracic acid enters into the total system in a proportion less than $\frac{2}{1000}$. With so feeble an amount, the law of dispersion peculiar to tartaric acid has already disappeared; and, for proportions of boracic acid ever so little stronger, if not for that very amount, the mode of dispersion re-enters into the general law, in which the deviations experienced by the planes of polarization of the various simple rays are sensibly reciprocal to the squares of the lengths of their fits.

62. To study these phænomena in their simplest phases, which hold out the expectation of discovering in them physical laws, I operated on systems such that the ponderable proportion of tartaric acid was always in a constant relation with the proportion of water, that of the boracic acid being the only variable element. It is therefore first necessary to state how such systems may be formed at pleasure.

Let A′ and A″ be two given aqueous solutions, the first of tartaric acid, the second of boracic acid, whose ponderable compositions are known and expressed as follows:—

Designation of the solution.	Proportion of acid in the unit of weight of the solution.	Proportion of water in the unit of weight of the solution.	Numerical relation of the two elements of each solution.
Tartaric solution A′	ε'	e'	$\varepsilon' + e' = 1$
Boracic solution A″	ε''	e''	$\varepsilon'' + e'' = 1$

It is required to compose with these two solutions a mixed

system in which the relation of the total amount of water to the tartaric acid is given and expressed by n, adding for this purpose, if necessary, a known weight of water. It is required, moreover, to assign the composition in weight of this new system, that is to say the proportions ε of tartaric acid, e of water, β of boracic acid which it contains in each unit of weight.

Let any weight T be taken of the tartaric solution A′, B of the boracic solution A″, E of additional water, giving for weight of the total system T + B + E. If T and B are decomposed into their respective constituent principles, and E be added, we shall have the constituent elements of the mixed system, as represented in the following table:

Weight employed of each partial system.	Absolute weight of acid.	Absolute weight of water.
Tartaric solution T ...	ε' T	e' T
Boracic solution B ...	ε'' B	e'' B
Additional water E ...	.....	E

Then the composition of the mixed system T + B + E will be as follows:

Proportion of tartaric acid in each unit of weight of the solution:

$$\varepsilon = \frac{\varepsilon' \mathrm{T}}{\mathrm{T} + \mathrm{B} + \mathrm{E}}.$$

Proportion of boracic acid in each unit of weight of the solution:

$$\beta = \frac{\varepsilon'' \mathrm{B}}{\mathrm{T} + \mathrm{B} + \mathrm{E}}.$$

Proportion of water in each unit of weight of the solution:

$$e = \frac{e' \mathrm{T} + e'' \mathrm{B} + \mathrm{E}}{\mathrm{T} + \mathrm{B} + \mathrm{E}};$$

which gives generally,

$$\varepsilon + \beta + e = 1.$$

Therefore, in order that e should be equal to $n\varepsilon$, as is required, it will be necessary to lay down the equation of condition

$$e' \mathrm{T} + e'' \mathrm{B} + \mathrm{E} = n\varepsilon' \mathrm{T},$$

whence we derive

$$\mathrm{E} = (n\varepsilon' - e') \mathrm{T} - e'' \mathrm{B},$$

in which we have always

$$\varepsilon' + e' = 1.$$

It is necessary that E should be positive, or at most null; for

if it were negative, this would indicate that some water must be removed from the mixture formed of the two solutions in order to obtain the constant relation desired, which, as it can only be effected by evaporation, would involve chances of inaccuracy, independently of the tediousness of the process. This inconvenience is avoided by employing tartaric acid in the solid state; for then, e' being null, ε' equal to 1, and the given multiple n an integer or fractional number always positive, we can always assume the weight T great enough that the product n T may surpass or equal e'' B. But, besides the time which complete liquefaction of the mixed system would require, we should always have to apprehend that it was not sufficiently charged or stable; and it is far more advantageous to have only to mix solutions already made. Fortunately the expression of E shows, that to be able to operate thus, it suffices to employ a tartaric solution sufficiently charged with acid for the factor $n\varepsilon' - e'$ to be positive. In fact, this being supposed, when a known weight T of this solution has been placed in a counterpoised phial, on the scale of the balance, we have only to add gradually weights B of the boracic solution, such that E may remain positive or become exactly null, according to its expression, which would leave only to dilute the system by this quantity of water E, to give it the proportions required by the relation n. And if this limit at which E is positive has been accidentally exceeded, from too much B of the boracic solution having been added, the equilibrium may always be re-established by a further small addition of the tartaric acid T. Now, the previous condition of $n\varepsilon' - e'$ positive is very easy of fulfilment; for, designating by n' the ponderable relation of water to the tartaric acid, in accordance with which this solution is made, there will result

$$\frac{e'}{\varepsilon'} = n';$$

and as we always have

$$e' + \varepsilon' = 1,$$

we deduce from these two equations,

$$\varepsilon' = \frac{1}{n' + 1}, \qquad e' = \frac{n'}{n' + 1};$$

which gives

$$n\varepsilon' - e' = \frac{n - n'}{n' + 1}.$$

Consequently, in order that the first member be positive, it is sufficient that n' should be less than n, that is to say, that the tartaric solution should be made with a less proportion of water than the ternary systems to be deduced from it, which it is always easy to effect. I can state, from numerous experiments, that the formation of successive ternary systems is obtained thus on the balance with facility and precision, within all the limits of the quantities which the solubility of the boracic acid admits under the circumstances of the experiment. I have always employed it thus, in the state of crystal, in the solutions B which I previously formed.

63. Supposing then a certain number of ternary systems into which this acid enters in various ponderable proportions β, from the weakest up to the strongest compatible with its actual solubility, with the condition that the relation $\frac{e}{\varepsilon}$ is constant in all and equal at η, we observe their respective densities δ, as well as the deviations α which they produce on a luminous ray of fixed refrangibility, for example, on the red ray through known thicknesses l, at a constant temperature. Then, in each series of systems to which n is common, the deviations α present constantly the following physical law.

For the sake of shortness, let

$$[\alpha] = \frac{\alpha}{l\varepsilon\delta};$$

we have always

$$[\alpha] = A + \frac{B\beta}{\beta + C}.$$

A, B, C are three constant coefficients, proper to each series, but which vary with the value of the relation n. In reality, B and C are the only ones which it is necessary to derive from the observations of each series. For the first A, corresponding to β null, expresses the value of $[\alpha]$, which results for a tartaric solution free from boracic acid, and constituted in the ponderable relation of water expressed by n. Now, this value has been previously determined for each temperature, according to the rectilinear or hyperbolic laws proper to this class of solutions, when their quantities are known. However, in the tables of experiments which I shall give further on, I have not wished to trust to this connexion, and I have preferred deducing the three coefficients A, B, C from observations in which β was not nul,

in order to obtain, as a verification and proof of continuity, the agreement of the constant A with the value of $[\alpha]$ proper to the pure tartaric solution. The exactitude of this agreement will be seen by the tables themselves.

64. If we consider generally $[\alpha]$ as the ordinate of a plane curve of which the abscissa is β, the relation here found between these two variables is constructed by an equilateral hyperbola, whose asymptotes are respectively parallel to the axes of the coordinates $[\alpha]$ and β, as is represented in Plate V. fig. 5. The centre C of this hyperbola is placed at the point whose abscissa OX is $\beta = -C$, and the ordinate CX $[\alpha] = A + B$; its summit S corresponds to the abscissa OH where $\beta = -C + \sqrt{BC}$; and it has for its ordinate HS, where $[\alpha] = A + B - \sqrt{BC}$. The point D, taken on the curve, for the abscissa $\beta = 0$, answers to the case in which the system contains no boracic acid; and thus the ordinate which corresponds to it is $[\alpha] = A$, that is to say, the primitive value of $[\alpha]$ for the pure tartaric solution. It is then, starting from this point D, that the hyperbolic relation begins to be realized by experiment, and only for positive values of β. Its physical application does not however extend indefinitely to all these values, because, from the nature of the problem, β, representing the ponderable proportion of boracic acid existing in the mixed system, should always remain less than unit, which is its extreme limit. The ordinate $[\alpha] = A + \frac{B}{1 + C}$, which answers to the abscissa $\beta = 1$, expresses therefore the greatest physical value which $[\alpha]$ can attain; and as the coefficient C is always a very small fraction, as will be seen in the tables, it is a little inferior to the final asymptotic ordinate $[\alpha] = A + B$, which is the geometrical limit of $[\alpha]$. But the slight solubility of the boracic acid, even under the influence of the tartaric acid, creates another material obstacle which renders the system of the three bodies impossible in the liquid state, for values of β much below the numerical limit $\beta = 1$. For, with far less values, at temperatures at which these experiments can be practically made, the proportions of the boracic solution which it would be requisite to introduce would precipitate their acid in the solid state, which interrupts abruptly the physical continuity of the results. It is for this reason that I have never been able to realize the hyperbola up to its summit S, so that only a very limited arc beyond the point D, corre-

sponding to the pure tartaric solution, can ever be obtained. Nevertheless, this length of arc enables us to establish indubitably, either graphically or by numbers, its curvature, as is proved in figs. 6, 7 and 8, Plate V., and in the tables relating to it at the end of this memoir, which present under the same form the results of three different series, made at temperatures scarcely different, with very dissimilar proportions of water, from the weakest values of β up to the greatest which the solubility of the boracic acid allowed of employing in each series without precipitation. The numerical coefficients of the three hyperbolas thus obtained are expressed in the following table, with the indication of the general circumstances proper to each series of observations which they represent.

Relation of the weight of water to that of the tartaric acid in all the solutions of each series. n.	Numerical coefficients of the equilateral hyperbola.			Mean temperature of the observations of each series.
	A.	B.	C.	t.
1·036666	7°·2661	143°·44690	0·28093240	+23°·8
3·000000	9·5830	70·32000	0·07538665	+23·4
5·000000	10·3336	51·88556	0·034308553	+21·5

65. The chance of the season, rather than an intentional foresight, admitted of these three series being effected at temperatures slightly different; and, fortunately, this phase of temperatures is precisely that in which the proper power of the tartaric acid is scarcely influenced by the variations of that element. The differences manifested in the coefficient A result from the changes which this power experiences according to the various proportions of water associated with that acid in the pure tartaric solutions, and they are there reproduced such as the immediate observation of these solutions had previously shown them to be, which proves the continuity of the results. With respect to the two other coefficients B and C, which depend on the reciprocal action exercised between each tartaric solution and the boracic acid introduced, it is immediately seen that their numerical values increase in proportion as the quantity of water n associated with the tartaric acid diminishes; but I am not acquainted with the precise law of these variations. Only it is evident, from the graphical delineation as well as from the numbers, that the realizable portion of the hyperbola is curved in proportion as the constant amount of water was greater in comparison

to that of the tartaric acid. It was almost rectilinear in the series where this proportion was nearly equal. Now, from what has been established in § 59 of the preceding section, this relation of equality was precisely that which gave to the group of tartaric acid and water its maximum of optical energy, at the temperature at which its combinations with the boracic acid were observed.

66. In the detailed table of each series I have, for brevity sake, called the quantity $[\alpha]$, or $\frac{\alpha}{l\varepsilon\delta}$, *the specific rotatory power of the tartaric acid*, and I have expressed its values for a length of 100 millimetres, as they are inferred from the hyperbolic law, taking into consideration the corresponding values given by observation. The mean difference of these two modes of evaluation is inappreciable. The preceding denomination of $[\alpha]$ applies to the tartaric acid alone the specific power actually exercised by any molecular group, which it forms with the two other elements of each solution. If it were desired to apply this denomination to the mixed group composed of water and of this acid which is supposed to combine with the boracic acid without decomposition, there would only result a proportional change in the absolute numerical values; but the physical law expressing their mutual dependence would remain the same. In fact, applying here the reasoning in § 20 of the first section, let $[\alpha]'$ be the *actual* molecular power of the group thus composed, when it has entered into combination with the boracic acid, and let us call $(\varepsilon)'$ its ponderable proportion in each unit of weight of the total system. We shall first have

$$(\varepsilon)' = \varepsilon + e;$$

or, since $e = n\varepsilon$,

$$(\varepsilon)' = (n+1)\varepsilon.$$

Now, if this group forms part of a system whose density is δ, and if it introduces into it the resulting power $[\alpha]'$ attributed to it, it will produce through the thickness l a total deviation expressed by $[\alpha]' l\delta(\varepsilon)'$, or $(n+1)[\alpha]' l\varepsilon\delta$. Then, if the deviation really observed is α, we conclude

$$(n+1)[\alpha]' = \frac{\alpha}{l\varepsilon\delta};$$

and since we have made

$$[\alpha] = \frac{\alpha}{l\varepsilon\delta},$$

there will result

$$(n+1)[\alpha]' = [\alpha].$$

According to this, having proved by experiment that, in each series in which n is constant, the $[\alpha]$ follow a hyperbolic law whose coefficients we determine, it is clear that the $[\alpha]'$ will also follow a similar law whose coefficients A and B will merely have a less value in the relation of $\frac{1}{1+n}$ to 1; so that the chemical group composed of tartaric acid and water having the molecular power $[\alpha]'$, offers, relatively to the ponderable proportion β of boracic acid present, a law of progressive connexion, analytically similar to that which the simple group of tartaric acid presents in the purely aqueous solutions of this acid, relatively to the ponderable proportion e of water with which it was then associated, as we have established in § 55 of the preceding section. For the hyperbola of fig. 5, Plate V., modified by the factor $\frac{1}{n+1}$ and the hyperbola of fig. 2, are both of the same nature, as well as both similarly placed and applied to the analogous elements of the two systems, whence it clearly results that their similar course represents similar phænomena of molecular reaction amongst different chemical groups. There is no dissimilarity except in the absolute values of the numerical elements.

67. Lastly, if we consider the mean group composed of tartaric acid and water, whose power is $[\alpha]'$, as forming with boracic acid a uniform combination indefinitely variable in proportion as the amount β of this latter acid increases, each mixed system thus constituted would realize the case of liquids chemically homogeneous which we have treated of in §§ 8 and 27 of the first section. Calling then $[\alpha]''$ the molecular rotatory power of the complex groups thus composed, we should have, as in the paragraphs cited,

$$[\alpha]'' = \frac{\alpha}{l\delta}.$$

Now, for each series of such systems, where the relation of the weight of water to that of the tartaric acid is n, experiment gives us the hyperbolic relation

$$\frac{\alpha}{l\varepsilon\delta} = A + \frac{B\beta}{\beta + C}, \quad \ldots\ldots \quad (H.)$$

A, B, C being three numerical coefficients, functions of n alone, and constants in one and the same series. There will therefore result

$$[\alpha]'' = \left[A + \frac{B\beta}{\beta + C}\right]\varepsilon.$$

But the three quantities ε, β, e, are connected by the general relation

$$\varepsilon + \beta + e = 1,$$

which, for the systems which we unite in one series, becomes

$$(n + 1)\varepsilon + \beta = 1,$$

whence

$$\varepsilon = \frac{1 - \beta}{n + 1}.$$

This value of ε being substituted in the expression of $[\alpha]''$, there finally results

$$(n + 1)[\alpha]'' = A(1 - \beta) + \frac{B\beta(1 - \beta)}{\beta + C}.$$

Thus, in each series of systems in which n is given, when the coefficients A, B, C of the hyperbolic relation proper to this series are known, we obtain by this formula the molecular power $[\alpha]''$ of the mixed group, composed of tartaric acid, water and boracic acid, which is realized for each ponderable proportion of this latter acid, expressed by the corresponding value attributed to β. The optical power of this group will vary therefore continuously in each series with this proportion; and it will moreover vary continuously from one series to another for one and the same value of β, according to the proportion of water associated with the tartaric acid, which is expressed by the number n, without these changes having other limits than the possibility of each system existing in the liquid state with the elements which constitute it.

From the general expression of $(n + 1)[\alpha]''$, we find that, in each series in which n is constant, the optical action of the complex group formed of tartaric acid, water and boracic acid, attains its maximum of energy when the ponderable proportion of this latter acid is such that we have

$$\beta = -C + \sqrt{\frac{BC(1 + C)}{A + B}};$$

but on substituting in this expression the values of A, B, C proper to each of our series, it is seen that the value of β, corresponding to the maximum which it indicates, cannot be realized

from the want of solubility of the boracic acid. In fact, the calculation thus carried out gives

For $n = 1{\cdot}03666$,	$\beta = 0{\cdot}30431$;
$n = 3{\cdot}0000$,	$\beta = 0{\cdot}19172$;
$n = 5{\cdot}0000$,	$\beta = 0{\cdot}13688$.

Now the greatest values of β, which I have been able to realize, are for the first series 0·094, for the second 0·0492, and for the third 0·0695,—all values very inferior to the preceding. In truth, I do not now recollect with certainty whether, in the second, I carried the experiments as far as the limit of precipitation of the boracic acid, and it is presumable that I did not. According to the values of β given by the formula, that is to say by the numerical law of the phænomenon, it is seen that the maximum of optical action of the complex group corresponds to a ponderable amount of boracic acid less, in proportion as the system contains more water, and consequently less tartaric acid, in the unit of weight. But probably this peculiarity depends on the temperature.

If these results be compared with those which we have already found for the simple aqueous solutions of tartaric acid, it will be perceived that the double mode of mutability noticed here is only an extension of that which we have there observed, and which is attributable to the greater complication of the ternary system considered. And we only find in it a simultaneous reaction of the three bodies presented to each other, producing in the whole mass of the system uniform chemical groups, perpetually varying in their material constitution as well as in their optical properties. The numerous experiments which I have related in vol. xvi. of the *Mémoires de l'Académie* on the liquid systems formed by tartaric acid and water with the earths and fixed alkalies, already led to this result; but I was not then able to follow so far the phases of their variations, nor to establish so precisely their physical laws as I have done here.

68. It remains for me to give some directions as to the course which should be followed to determine easily the constants A, B, C, which characterize the hyperbolic law proper to each series in which the relation n of the water to the tartaric acid has the same value. Representing then, as previously, by $[\alpha]$ the function $\frac{\alpha}{l\,\varepsilon\,\delta}$, which is the ordinate of the hyperbola correspond-

ing to the abscissa β, we have

$$[\alpha] = A + \frac{B\beta}{\beta + C}. \quad \ldots \quad (H.)$$

The operation becomes very easy if we employ, as given, the value of $[\alpha]$ furnished by the observation of the pure tartaric solution. In fact, β being then null, this value of $[\alpha]$ should be equal to the constant A which is determined by this condition. A being thus known, I put the equation in the form

$$\{[\alpha] - A\}\beta + \{[\alpha] - A\}C = B\beta.$$

Let us designate by $[\alpha]_2$, β_2, $[\alpha]_3$, β_3, the simultaneous values of $[\alpha]$ and of β, relative to two other observations of the same series, in which they have been determined experimentally. Each of these pairs should satisfy the preceding relation, which will furnish the two conditions

$$\{[\alpha]_2 - A\}\beta_2 + \{[\alpha]_2 - A\}C = B\beta_2;$$
$$\{[\alpha]_3 - A\}\beta_3 + \{[\alpha]_3 - A\}C = B\beta_3.$$

All is known in these equations excepting B and C; and these quantities both enter in the linear form. We may therefore easily deduce them by elimination; and on associating them with the value already obtained of A, we obtain the three constants of the series. We then calculate the values of $[\alpha]$ by those of β for the other observations made; and on comparing them with the $[\alpha]$ observed, we shall prove the accuracy of the hyperbolic law which connects them.

69. But, when we do not wish to employ the observation of the pure tartaric solution to determine directly the constant A, in order to deduce from the law itself the corresponding value of $[\alpha]$, the equation (H.) must be subjected to a preliminary transformation, so as to avoid radicals. For this purpose, I change the product $B\beta$ into its equivalent $B(\beta + C - C)$; and on effecting the divison by $\beta + C$ on the two first terms, I obtain

$$[\alpha] = A + B - \frac{BC}{\beta + C}.$$

Then substituting new letters to represent the coefficients thus grouped, I make

$$A + B = a; \qquad BC = b; \qquad C = c;$$

which gives

$$[\alpha] = a - \frac{b}{\beta + c},$$

and consequently

$$\{[\alpha] - a\}\{\beta + c\} = -b.$$

When we have determined the new constants a, b, c, we immediately deduce A, B, C from their relations with them. I have merely changed C into c to complete the analogy of the new notation.

Let us take now, in the series of one system of solutions, three pairs of simultaneous values $[\alpha]_1, \beta_1$; $[\alpha]_2, \beta_2$; $[\alpha]_3, \beta_3$, for each of which we have determined, from observation, the value of $[\alpha]$ corresponding to that of β. These pairs ought to satisfy the hyperbolic relation. We shall therefore have

$$\{[\alpha]_1 - a\}\{\beta_1 + c\} = -b;$$
$$\{[\alpha]_2 - a\}\{\beta_2 + c\} = -b;$$
$$\{[\alpha]_3 - a\}\{\beta_3 + c\} = -b.$$

And since the first members are equal to the same quantity $-b$, we have, on equating them,

$$\{[\alpha]_2 - a\}\{\beta_2 + c\} = \{[\alpha]_1 - a\}\{\beta_1 + c\};$$
$$\{[\alpha]_3 - a\}\{\beta_3 + c\} = \{[\alpha]_1 - a\}\{\beta_1 + c\}.$$

On developing the multiplications indicated, the product $a\,c$ disappears from each of these equations; and it is in this that the simplification consists. Then there remains

$$0 = [\alpha]_3\beta_2 - [\alpha]_1\beta_1 + \{[\alpha]_2 - [\alpha]_1\}c - (\beta_2 - \beta_1)a;$$
$$0 = [\alpha]_3\beta_3 - [\alpha]_1\beta_1 + \{[\alpha]_3 - [\alpha]_1\}c - (\beta_3 - \beta_1)a.$$

All is now known in these two equations, except the constants a and c which occur in the linear form. They may therefore be easily deduced by elimination when all the terms associated with them have been converted into numbers. a and c being thus obtained, we have b by any one of the three equations expressing it, and we may thus verify the accuracy of the calculations by their agreement. And thence we lastly deduce the values of the primitive constants A, B, C, which will be

$$A = a - \frac{b}{c}, \qquad B = \frac{b}{c}, \qquad C = c.$$

Such is the simplest and safest method to calculate them accurately.

Conclusions.

70. In the first section of this memoir I have established, by reasoning and by experiment, the characters of the action which the molecules of a great number of substances exercise upon polarized light; and I have deduced from them formulæ which express all the optical effects which substances thus constituted should produce, on a polarized ray traversing sensible thicknesses of them, when they are either in a complete state of disaggregation, or in a confused state of aggregation, which permits the action of their molecules to be freely manifested. I have then explained the processes by which these molecular phænomena are distinguished from similar appearances, which may be produced by special circumstances of aggregation, such as takes place in regularly crystallized quartz, when the light traverses it in the direction of its axis of double refraction. It is to be remarked that, hitherto, the molecular action in question has been observed only in substances, or in combinations containing at least one organic element.

71. In the second section I have confirmed these considerations by a class of facts of a wholly different nature. I have shown that, when substances possessing a molecular rotatory power are mixed or combined in the liquid state with inactive bodies, the resultants of action exercised upon polarized light by these mixed systems, in the one or other state, are exactly in accordance with the relations of variation observed between their densities and those of the primitive systems from which they are derived, the comparison being made at one and the same temperature; so that the same consequences are deduced as to the actual state of combination or non-combination of the systems thus formed.

72. In the third section I have applied these principles to the optical effects produced on polarized light by the aqueous solutions of tartaric acid, of various strengths, either observed pure or associated with other substances in the liquid state, and I have established the numerical laws to which the succession of these phænomena is subjected. In pure aqueous solutions, I have proved that the acid is not merely mixed with the water, but that it forms with the entire mass of that liquid presented to it a uniform combination, in proportions continually variable with the strength, so that the action thus exerted by each

particle of acid is propagated indefinitely to all the particles of water surrounding it, either directly, or by communication, like magnetic action, and like that, with an energy decreasing in proportion as the mass of water affected augments, without limit.

73. Lastly, in the fourth section I have considered the effects produced by aqueous solutions of tartaric acid of constant strengths, when gradually increasing quantities of boracic acid are successively introduced. I have shown that, in this case again, the primitive aqueous solution combines entirely with the boracic acid introduced, forming with it a uniform ternary system, of proportions continuously variable, whose progressive change, indicated by the optical effects, follows laws similar to those which the progressive combinations of tartaric acid with water alone had presented.

74. These experiments, joined to many others which I have inserted in the *Mémoires* and the *Comptes Rendus des Séances de l'Académie des Sciences*, or which have been made by different observers, evidently show, I think, how much the observation of the molecular rotatory powers may serve to throw light upon the most abstract questions of chemical mechanics, which have hitherto evaded every experimental process. Thus, in many cases, it furnishes distinctive molecular characters, not less evident than certain, between substances which appear exactly isomeric when merely compared by the analyses of their sensible masses. What is there more marked, for example, than the distinction of tartaric acid and paratartaric acid; the first acting by rotation on polarized light, and carrying this power into all the combinations into which it enters; while the second, either isolated or combined, is absolutely without action? The essential oils and their chemical modifications present a multitude of similar cases.

75. Again, we owe to optical processes our first accurate notions respecting the nature of the substance constituting the kinds of starch which may be extracted from the cellular tissue of a great number of vegetables, and respecting the progress of the chemical changes which it may be made to undergo artificially. When these pulverulent products are observed under the microscope, between two of Nicol's prisms, whose principal sections are at right angles, especially if their action on polarized light is rendered more manifest by the interposition

of a *sensible* plate of gypsum, they are seen to consist of a heap of ovoïdal globules, composed of solid, transparent strata, intimately superposed, but distinguished by their peculiar densities or by their mode of apposition, and constituted by meridional sections around a point of the superficies of the globule called the umbilicus, in the same manner as the sides of a pear or the zones of a melon are arranged around the peduncle through which they derive their nutriment. And, further, this structure is locally fixed as in the above fruits; for the effects which it produces on polarized light subsist without modification in each fragment of a broken globule*. As long as these preserve their natural state

* To make these observations, I employ an achromatic microscope, containing a small Nicol's prism fixed behind the object-glass on the side of the eye-glass. I insert some particles of starch in a thin layer of water contained between two glasses, one of which is plane, and the other slightly concave internally, but plane without. When this system has been placed on the stage and brought into focus, I place above it a second Nicol's prism, which is inserted in a ring centred on the axis of the incident pencil, and I turn this prism on itself, until, by the perpendicularity of its principal section to that of the other prism behind the object-glass, the field of vision becomes completely black in all the parts where the course of the luminous rays is not interrupted by the starch globules. Then, each of the luminous pencils which traverses these globules undergoes a deplacement of its plane of polarization, which shows their form, and gives them the appearance indicated in the text. If the starch is fresh, we generally perceive in each globule a black cross, the arms of which intersect in its umbilicus, and appear straight or curved, according as the axis of the globule is presented straight or obliquely to the eye. These appearances are especially regular when the starch has been previously washed with cold water slightly acidulated with one- or two-thousandth parts of hydrochloric acid, which cleans the surface of the globules of any organic matters which often adhere to them, and which may be produced, either by ruptures of the cellular membranes enclosing them, or by their mutual friction in preparing them. But when the starch is old, the globules are generally deformed and rugose, which produces the appearance of unequal sectors having nevertheless always the umbilicus for their summit. These phænomena of polarization are manifested in the same manner and with similar characters in all the starches, the smallest as well as the largest. But they are more energetic in proportion as the volume of the globules is more considerable; and in a great number their intensity is such as to produce colours analogous to those of plates of alum, excepting that the outlines of the coloured portions are curved, because they follow the inflexions of the tangent plane at each division of the surface of the globules. They subsist in each portion of the globule accidentally broken, as if it were entire; and when two or more globules are naturally connected together, which often happens in the large kinds, each individual still produces them around its own axis. These characters of direction relative to meridional planes could evidently not result from the existence of an interior liquid: they can only belong to a system regularly aggregated by organization. The lamellar character of this kind of action is manifested likewise by the modifications it produces in the proper colours of thin crystallized laminæ interposed in the passage of the rays, posteriorly to the first prism. To make these effects most manifest, a thin lamina of gypsum should be selected, whose thickness is such, that its extraordinary tint is Newton's violaceous purple-gray of flax, which answers in his

of aggregation, they are not soluble in water; but sulphuric, nitric, hydrochloric, oxalic, and probably many other acids (from which however acetic acid must be excepted), disintegrate their constituent particles, in the cold when they are very concentrated, or even in a state of very great dilution when the action of these solvents is aided by a slight elevation of temperature, or by heat and pressure in the autoclave*. This disaggregation is gradual; and in proportion as it is more or less advanced, the disunited portions remain a longer or shorter time in suspension, or dissolved in the water in presence of the acid, or even after the latter has been saturated by an alkali, especially if the salt formed is not precipitable; and we arrive at last at such a degree of tenuity that the disaggregated substance may remain suspended indefinitely, even in pure water, after all the acid has been separated. These fragments of the primitive globule appear, according to their degree of attenuation and disorganization, more or less complete, also more or less susceptible of being tinted by iodine, which colours, as is well known, natural starch blue, when held in a state of precipitation in water at temperatures below 100°; and the tints they assume vary according to these two peculiarities of condition. So that, on breaking up the starch globules by mechanical trituration, some fragments may be removed from them by cold water, still organized, although so minute that they remain suspended in this liquid as in a true solution, which, when cold, is coloured blue by iodine, and is deprived of colour by an elevation of temperature below 100°, and again assumes its colour spontaneously on cooling, if precautions have been taken to prevent the whole of the iodine being vaporized†. But all these changes are purely physical; for, as

table of the thicknesses of the laminæ of air to the number 21·5, because it is there that the change of the tints is most rapid, passing by the least subtractive action into red, and by the least additive action into green. This is what I have called, in my experiments on lamellar phænomena, *la lame sensible*. By interposing it, as I have said, in the passage of the rays between the crossed prisms, all the sectors which appeared white before its interposition become alternately red, yellow, blue, or green, according to the direction of the tangent plane; and their combination, in the field of vision, presents one of the most curious physical spectacles which can be seen.

* This last experiment is due to M. Jacquelain, assistant at l'Ecole Centrale des Travaux Publics; he thus disaggregated the starch, and converted it into soluble dextrine, by the action of water to which $\frac{2}{1000}$ of oxalic acid had been added, by raising the temperature sufficiently in closed vessels.

† This curious experiment was described by M. Lassaigne in the *Journal de Chimie Médicale*, vol. ix. p. 651, of the year 1833. I have preserved for some years a flask with a ground stopper filled with an aqueous solution of starch

soon as the starch matter has been sufficiently disaggregated to remain, even temporarily, in suspension or in solution in water, whether pure or mixed with acids, it manifests a constant, very

and iodine possessing these properties of mutability, and which was presented to me by M. Lassaigne himself. He had prepared it by pouring 3 decilitres of cold water upon 0·4 gramme of triturated starch, and filtering the mixture in order to separate the portion which had become soluble, then adding 30 decilitres of an aqueous solution of iodine. This mixture, at first blue, lost its colour upon a suitable elevation of temperature, and again became blue on cooling; it preserved this last tint constantly for several years, remaining at the same time perfectly limpid. Having lately submitted it to the same trials in a water-bath heated progressively, the flask being only half-open, the blue colour disappeared long before the bath approached the boiling-point, and it was not restored by cooling. But the cooled liquid immediately acquired a blue colour by a new addition of alcoholic tincture of iodine. And if this addition was made while it was hot, it acquired only a yellow tint, which gradually became blue as the temperature lowered. I took advantage of its decoloration to observe its optical power in a tube of 500 millimetres. It did not produce any appreciable deviation through this length, whence I conclude that the ponderable proportion of dissolved dextrine was less than $\frac{1}{1000}$; which shows at the same time the excessively small quantity of soluble matter which cold water is capable of removing from triturated starch, and the excessive sensibility of the chemical test which renders such small quantities evident from the colour it imparts to them. However, this colorization is no longer effected thus when the organization of the granules of which the starch globules are composed has been completely destroyed. For syrup of dextrine, prepared by means of sulphuric acid, then separated from this acid by saturation, is no longer coloured blue by the tincture of iodine, whether hot or cold. It only takes a yellow tint more or less reddish, although it contains a considerable quantity of dextrine, that is to say, of starch completely disaggregated and reduced to the molecular state, which is manifested both by the great energy of its rotatory power and by the precipitation which alcohol causes in it. To observe the succession of tints which starch acquires from the iodine in the various phases of its disintegration, whether mechanical or chemical, I arrange a microscope so that the end of the tube which bears the object-glass may be turned upwards, and that the luminous pencils traverse it from above downwards, and are then brought horizontally towards the eye by total reflexion in an interior prism. Then I place a polished and thin watch-glass upon the stage, which now occupies the uppermost position, into which I pour some water which forms a meniscus, and into this water I add the grains of starch, whole or broken, which falling to the bottom become observable underneath through the glass. Two metallic arms, forming part of the stage, and extending laterally, bear at their extremities two small spirit-lamps, which raise at will their temperature, and transmit it to the small glass containing the water, which may thus be brought gradually to the boiling-point. By this means the expansion and progressive disaggregation of the starch globules may be observed according as they are effected. They are seen to separate into flakes and into granules; and on adding a little solution of iodine, the progressive diversity of the tints which it gives to all these parts, according to their thickness and state of aggregation, is perceptible. We may, with the same apparatus, study the progressive action of alkalies and acids on the starch globules, on introducing these agents in quantities as small as we please. And without doubt it might also be employed to observe the progress of a multitude of chemical reactions, whose phases of mutation it would be very interesting to investigate. These various additions to the microscope have been very ably effected by M. Ch. Chevallier.

energetic rotatory power, proportional to its mass, and directed towards the right of the observer; a fact which led M. Persoz and myself to give it the denomination of *dextrine* when we had isolated it, and ascertained this character *. But the proportionality of the optical action to the active mass dissolved, as long as it exists, attests a constant molecular state. Now the following experiment is sufficient to establish this permanence of molecular action in all the degrees of attenuation which the substance composing the globules may admit. If, by degrees, a sufficient quantity of very concentrated nitric acid be poured over some starch in a glass mortar, disaggregating the lumps by continued trituration in order to render the action of the acid uniform and general, we obtain, after some instants, a diaphanous liquid, which, on mixture with water, deposits a white powder, which M. Braconnot, who first obtained it, has named *xyloidine*, and which M. Pelouze has found to contain the elements of nitric acid, joined or combined with those of the starch †. But, the

* *Researches on the modifications which starch and gum experience under the influence of acids.* (*Mémoires de l'Académie des Sciences*, vol. xiii.) In this memoir, which was drawn up by M. Persoz and myself, we have studied the progress of disaggregation of starch under the influence of water and acids aided by heat, from the moment when the system becomes completely fluid, to that at which the starchy substance is converted into fermentable sugar, which takes place by a sudden transformation accompanied by a considerable diminution of the rotatory power. I have since added to this investigation some experiments made with a view to prove directly the exact identity of the active substance thus obtained by disaggregation, under the influence of various acids. They consist first in forming with each of them aqueous solutions the strengths of which have been accurately ascertained. Then having taken known weights of each, in counterpoised phials, ascertained weights of the same starch taken in an hygrometric state common to all its parts are introduced, and the temperature of these systems is slowly raised to the precise point of their liquefaction, and the small quantity of water removed by evaporation is restored on the balance, or the diminution of weight is estimated and taken into account in the calculation, which comes to the same thing. The optical effect of these solutions is now observed in tubes of a known length, and their densities likewise measured at the same temperature; and from these elements we conclude the proper rotatory power of the starchy substance they contain. We find it the same for all, whatever acid be employed, provided that we stop carefully at the precise limit of liquefaction, so that no portion of the matter employed has passed into the state of sugar; or that if such an alteration has taken place in some of the particles, which it is very difficult to avoid, their weight at least may be insensible in comparison to the total mass employed. I have published these experiments in the journal *L'Institut*, vol. iii. page 13; but it is desirable that they should be repeated, as they might be now, with more precision and generality.

† *De la transformation de plusieurs substances végétales en un principe nouveau*, by M. Braconnot (*Annales de Chimie et de Physique*, 2nd Series, vol. lii. page 290). This memoir is anterior to the researches mentioned in the

longer it stands the more the precipitation produced by the water diminishes, and at length it ceases entirely, after which the liquid remains for some time limpid; then it becomes coloured more and more, and finally there are formed in it various products which have not yet been completely studied. But, up to this last phase of the chemical reaction, the starch has only become progressively disaggregated without changing its molecular state. For if the solution be taken as soon as it has become quite liquid, and a glass tube closed at its extremities by parallel glasses be filled with it, and this transferred upon the polarizing apparatus, it is found to possess a considerable rotatory power, directed like that of the dextrine towards the right of the observer; and this power remains exactly constant for several days, notwithstanding all the variations which the substance undergoes during this interval in its power of being precipitated by water. This proves therefore the constancy of its molecular state throughout this diversity of physical phases. Thus, during the whole time that it undergoes them, if we collect the precipitate formed by the water and observe it under the microscope, we discover in it the fragments of the starch progressively lacerated by the acids impregnating them, and mixed with a multitude of granules of dimensions still perceptible. Even when the reaction is not far advanced, if Nicol's prisms crossed rectangularly be used in the observation, and combined with a *sensible* lamina of gypsum, we see several of the shreds, and the larger granules themselves, still preserve their primitive organization so slightly modified as to act visibly on polarized light, and change the proper tint of the lamina into red or green. These phænomena only cease with the precipitation by water; and it is likewise then that the rotatory power commences to change perceptibly, the acid having sufficiently disaggregated the substance of the starch globules to modify its chemical na-

preceding note. At the time when it was composed, it was not known what use might be made of the rotatory power, as a molecular character of bodies possessing it. If the author had been able to apply this process of observation to the substance he obtained by acting with concentrated nitric acid on starch, lignine, cotton, or hemp linen, he would easily have ascertained that it was not produced, but only extracted from those bodies in a state of disaggregation, which modified merely its physical properties without changing its molecular condition, and that it was nothing else than the element of the starch globules contained in them. The important remark of M. Pelouze on the simultaneous presence of the two elements of the system in the matter precipitated by the water, is given in a note inserted in the *Comptes Rendus de l'Académie des Sciences*, vol. vii. p. 713.

ture. When this reaction is effected at a moderate temperature, for example between 15° and 20° C., it is progressive; that is to say, it does not operate instantaneously on the whole active mass, as may be ascertained by the gradual diminution of the rotatory power, as also because the rest of the active substance is still precipitable, no longer by water, but by alcohol; and we may easily prove also that, even in these advanced stages of the action, the property of acting on polarized light belongs exclusively to those starch molecules which are not yet destroyed. For if the acid be saturated by the addition of an alkaline solution, introduced into the mixed liquid, in a known proportion by volume, the rotatory power is seen to preserve the same intensity as before; and, on evaporating slowly the solution at a gentle heat, we obtain a true salt, which, redissolved, again exhibits the rotatory power. But besides its alkaline and acid elements, this salt is mixed with dextrine which the solution still contained. Thus it can never be made to crystallize in this mixed state, and this can only be effected by purifying it of that substance. At the end of this memoir will be found two tables of experiments in which the progress of the phænomenon was followed in all its stages, as long as the liquid formed could be observed by transmitted light.

76. The rotatory phænomena have served in medicine as a certain and readily applicable diagnostic for ascertaining the existence and appreciating the different stages of that dreadful disease called saccharine diabetes, by showing in a moment the absolute quantity of sugar actually contained in the urines at all stages of the disease, and at all the periods of medical treatment opposed to it*. Another observation, which may also be very useful, is that by which M. Bouchardat discovered that all the vegetable alkalies possess rotatory powers, of various directions and intensities†. For not only will this property serve to characterize them visibly, and enable us to ascertain with facility all the adulterations to which they may have been subjected, but moreover, the temporary or lasting modifications which they experience from the other alkalies and acids, as well as the various combinations into which they may be made to enter without de-

* *Comptes Rendus de l'Académie des Sciences*, tome xi. p. 1028. For the quantitative estimation of the saccharine matter, see vol. xv. pp. 633, 634.

† *Sur les propriétés optiques des alcalis végétaux*, by M. Bouchardat. (*Annales de Chimie et de Physique*, 3rd Series, vol. ix. p. 213.)

composition, will furnish a multitude of important experiments for explaining the molecular mechanism of chemical actions. If I am not deceived as to the tendency of these phænomena, they open a field of research among the most important as well as the most fruitful on which a chemist can enter.

Lastly, the same processes have already been employed to follow the progress of the natural juices of vegetables in the various parts of their organs, taking as a guide the modifications undergone by the saccharine matters which these juices contain, in proportion as they are carried in the progress of vegetation from the roots into the trunk, from the trunk into the leaves, and as they redescend from these latter in the exterior canals near the surface, where the new ligneous layers are formed. I give here, in a note, the indication of several researches of this kind which have been already published; but I present them less as finished investigations, than as essays, which deserve to be continued and still further extended*.

77. I will mention, in conclusion, that, according to the experiments made by M. Melloni and myself, some years ago, the rotatory properties of rock-crystal are exerted also upon the calorific rays, and impart to them deviations of the same direction as to the luminous rays, that is to say, directed in the same way for each plate toward the right or left of the observer. By a necessary consequence of this property, when various plates of quartz, perpendicular to the axis of crystallization, are interposed simultaneously, and in succession, in one and the same calorific beam previously polarized, their individual effects are added or compensated, according as the direction of their action is similar or contrary. These experiments have been described in the *Comptes Rendus de l'Académie des Sciences*, t. ii. p. 194; but we have not ascertained whether the same property of modi-

* *Journal de l'Institut*: Sur quelques nouveaux faits pour servir à l'histoire de la végétation, tome i. p. 229. Description d'un appareil à double effet pour observer les mouvemens de la sève ascendante et la recueillir, tome ii. pp. 66 and 222. *Nouvelles Annales du Muséum d'Histoire Naturelle*: Sur le mouvement et la nature de la sève de printemps, tome ii. p. 271. Sur les variations lentes ou soudaines qui s'opèrent dans les combinaisons organiques, tome ii. p. 335. Sur les transformations opérées par la vie végétale dans les produits carbonisés qui servent d'aliment aux jeunes individus, tome ii. p. 365. Sur l'application de la polarisation circulaire à l'analyse de la végétation des graminées, tome iii. p. 47. [A translation of this memoir, together with the observations of M. Chevreul on the same subject, will be found at p. 584 of the first volume of this work.] *Comptes Rendus de l'Académie des Sciences*: Remarques et expériences de physique végétale, à l'occasion d'une Lettre sur la filtration des liquides à travers les tiges ligneuses, t. xii. p. 357.

fying calorific rays existed for liquids exercising a rotatory power on polarized light; and it would be very interesting to ascertain the identity or the dissimilarity of the action in this latter case, where it is purely molecular.

Tables containing the results of two experiments, in which the progress of the reaction of concentrated nitric acid on the starch, in closed vessels, was continued during several days.

First Experiment.—The mixture was made on the morning of Monday, April 8th, 1844, by M. Pelouze, with some starch of commerce and very concentrated fuming nitric acid. As soon as the liquefaction appeared sufficient, the decanted solution was introduced into a glass tube whose length was $146^{mm}\cdot25$, and which was closed by thin glasses with parallel faces. It was nine o'clock in the morning. Through this thickness it appeared slightly turbid. Nevertheless its action on polarized light was distinguishable, and the deviation which it produced in the planes of polarization was estimated, by approximation, at between $+20^{\circ}\cdot5$ and $+21^{\circ}\cdot5$ towards the right of the observer. The rest of the solution was preserved in a flask with ground stopper, under conditions of temperature similar to those to which the tube was exposed; and this reserved portion was used to replace at need the small portion of liquid dissipated by evaporation at the surfaces of junction of the glasses, or to enable us to follow its action in other tubes a little different in length, when the corrosion of the metallic envelopes required this change. But all these results have been rendered comparable by reducing them, by the law of proportionality, to what they would have been in the primitive tube. As the especial object was to follow the progress of the reaction, and not to determine its precise course, the deviations were not observed through red glass, which would have been tedious and difficult, but only determined by the naked eye, by the passage of the extraordinary image from the vanishing blue tint to the rising yellowish red, adding the indication of the actual tint of the liquid observed. This renders the measurement of the deviations thus obtained relatively a little too small in proportion as the tint of the liquid is a deeper red. But this relative inferiority will only render in the present case more sensible the slowness of the molecular modifications experienced by the substance of the starch on which the acid acts.

Days and hours of the observations. April 1844.	Deviation observed with the naked eye, and reduced to a common thickness of 146mm·25.	Colour of the liquid in the tube of observation.	Various remarks.
h m			
Monday, 8 ... 10 0 in the morning.	+21°·95	Greenish yellow.....	The solution is still a little turbid, it is precipitated by water.
Id. ..... 11 45 in the morning.	21·91	Greenish yellow.....	Vision much better, but the liquor is still a little turbid.
Id. ..... 4 30 in the evening.	21·75	Greenish yellow.....	The same. Precipitated by water.
Tuesday, 9 ... 8 30 in the morning.	21·50	Yellow less greenish	Liquor more clear; precipitated by water. The precipitate, seen with a polarizing microscope, is composed of shreds of starch and of a multitude of starch granules; some still preserving sufficiently their organization to modify the proper tint of the sensible lamina, to red and to green.
Id. ..... 11 0 in the morning.	21·50	Yellow less greenish.	Temperature 19°. Through a yellow test-glass the deviation is +19°·5.
Id. ..... 4 0 in the evening.	21·00	Golden yellow	Precipitated by water.
Wednesday, 10 8 0 in the morning.	20·50	Orange yellow	Through a yellow test-glass the deviation is +18°·25.
Id. ..... 11 0 in the morning.	19·50	Orange	
Id. ..... 4 0 in the evening.	19·50	Reddish orange.	
Thursday, 11 10 0 in the morning.	18·56	Very dark reddish orange.	The solution no longer precipitated by water.
Id. ..... 12 30 in the evening.	18·31		
Id. 4 0 in the evening.	17·32	Orange red.....	Through a yellow test-glass the deviation is +16°·37.
Friday, 12..... 11 0 in the morning.	17·00	Orange red.....	Is not precipitated at all by water.
Id. ..... 4 0 in the evening.	16·50	Orange red.	
Monday, 25 ... 11 0 in the morning.	13·86	Orange red.....	The vision is no longer possible through the thickness of 146mm·25. We are obliged to make the observation in a tube of 99mm·2, in which the liquid appears of a dark orange tint. The deviation there is +9°·4, which gives 13°·86 in 146·25. The solution is no longer precipitated by water, but is so by alcohol, which is a property of dextrine, that is to say, to starch brought to the highest point of molecular disaggregation.

If we take into consideration the progressive change of the colour of the liquid, we see, by the numbers of this table, that the rotatory power of the active substance remained sensibly constant from the first instant of liquefaction until Thursday 11, when the molecular disaggregation of the starch was sufficiently complete for the precipitation in water no longer to take place. But the progressive weakening of the rotatory power, commencing at this point, shows that the acid had begun to alter gradually the constituent molecules of the starch, and to change it into another product of smaller, or perhaps inverse rotatory power. To follow further this reaction, and to determine its final product, it would be necessary to make the experiment on masses whose elements were determined by weight, and to examine the properties, both chemical and physical, of the result of the transformation; but this research can only be successfully undertaken with the aid of chemical knowledge, which I should not have been able to bring to it.

TABLE I.—*Results of Optical Observations made in* 1836 *on Tartro-boracic Solutions formed in the constant proportion of* 1·03666 *part by weight of water to* 1 *part of tartaric acid.*

Date of the experiment.	Proportion of tartaric acid in the unit of weight of the solution. s.	Proportion of water. e.	Sum of the weights of water and tartaric acid. $e+s$.	Ratio of the weight of the water to that of the tartaric acid. $\frac{e}{s}$.	Proportion of boracic acid in the unit of weight of the solution. β.	Temperature at which the deviations were observed.	Temperature at which the densities were determined.	Specific densities of the solutions corrected for the dilatation of the water. δ.	Specific rotatory power of tartaric acid on the red ray, calculated for a thickness of 100mm, $\frac{\alpha}{l_{100}\delta}$. Calc. by the hyperbola.	Specific rotatory power of tartaric acid on the red ray, calculated for a thickness of 100mm, $\frac{\alpha}{l_{100}\delta}$. Observed.	Excess of the power calculated by the hyperbola over that obtained by direct observation.	
1836	0·4910000	0·5090000	1·0000000	1·03666	0·00000000	25°·0	23°·0	1·257614	7°·26610	7°·63096	−0°·36486	
	0·4903527	0·5083290	0·9986817	1·03666	0·00131778	22·9	23·0	1·257778	7·93590	7·94092	−0·00502	Given by hyp.
	0·4892964	0·5072340	0·9965304	1·03666	0·00346993	26·0	23·0	1·25686	9·01630	9·06823	−0·05193	
	0·4865600	0·5043965	0·9909565	1·03666	0·00904350	22·4	23·0	1·25831	11·73950	11·43255	+0·30695	
	0·4793235	0·4969173	0·9762408	1·03670	0·0237592	23·0	19·0	1·26253	18·4487	18·2946	+0·15410	
	0·4741000	0·4915181	0·9656181	1·03674	0·0343816	22·0	21·2	1·26265	22·9034	22·91154	−0·0080	Given by hyp.
	0·4577796	0·4746528	0·9324324	1·03686	0·0675676	24·0	19·0	1·27027	35·1046	35·5215	−0·4169	
	0·4456590	0·4621208	0·9077798	1·03694	0·0922203	22·0	21·4	1·27280	42·7179	42·72024	−0·0023	Given by hyp.
	0·4448400	0·4611470	0·9059870	1·03666	0·0940086	23·8	22·8	1·27026	43·2324	42·4279	+0·8045	

Equation of the hyperbola $\frac{\alpha}{l_{100}\delta} = 7°·2661 + \frac{143°·4469\,\beta}{\beta + 0·2809324}$.

Sum of the positive deviations ... +1·26555
Sum of the negative deviations ... −0·84901
Total sum of the deviations ..... +0·41654
Mean deviation $\frac{1}{9}$ ..... +0·04628 { Scarcely perceptible.

Obs.—The slight inaccuracies in the reproduction of the data employed are owing to the numerical difficulties which occur in the determination of the coefficients of the hyperbola, owing to the smallness of the curvature of the arc included by the observations.

TABLE II.—*Results of Optical Observations made in* 1837 *on Tartro-boracic Solutions formed in the constant proportion of* 3 *parts by weight of water to* 1 *part of tartaric acid.*

Date of the experiment.	Proportion of tartaric acid in the unit of weight of the solution. t.	Proportion of water. e.	Sum of the weights of water and tartaric acid. $e+t$.	Ratio of the weight of the water to that of the tartaric acid. $\frac{e}{t}$.	Proportion of boracic acid in the unit of weight of the solution. β.	Temperature at which the deviations were observed.	Temperature at which the densities were determined.	Specific densities of the solutions corrected for the dilatation of the water. δ.	Specific rotatory power of tartaric acid on the red ray, calculated for a thickness of 100mm. $\frac{\alpha}{l\,t\,\delta}$. Calculated by the hyperbola.	Observed.	Excess of the power calculated by the hyperbola over that obtained by direct observation.	
1837	0·2500000	0·750000	1·0000000	3·0000	0·0000000	24°·0	21°·8	1·12030	9°·5830	9°·8636	−0°·2806	
	0·2497702	0·7495600	0·9993302	3·0010	0·0006694	22·5	21·8	1·12150	10·2019	10·20187	0·0000	Given by hyp.
	0·24951075	0·74872035	0·9982311	3·00075	0·00176945	23·0	23·5	1·12171	11·2046	11·0406	+0·1640	
	0·2469341	0·7408363	0·9877604	3·0001	0·0122401	24·0	22·0	1·12384	19·4056	19·4056	0·0000	Given by hyp.
	0·237701	0·713103	0·950804	3·0000	0·0491960	23·5	23·0	1·132075	37·3514	37·3514	0·0000	Given by hyp.
Equation of the hyperbola $\frac{\alpha}{l\,t\,\delta} = 9°·5830 + \frac{70°·3200\,\beta}{\beta + 0·07538665}$.											Total sum of the deviations, both positive and negative...	−0·1166	
											Mean deviation $\frac{1}{5}$	−0·0233	Imperceptible.

TABLE III.—*Results of Optical Observations made in* 1835 *and* 1836 *on Tartro-boracic Solutions formed in the constant proportions of* 5 *parts by weight of water to* 1 *part of tartaric acid.*

Date of the experiments.	Proportion of tartaric acid in the unit of weight of the solution. ι.	Proportion of water. e.	Sum of the weights of water and tartaric acid. $e+\iota$.	Ratio of the weight of the water to that of the tartaric acid. $\frac{e}{\iota}$.	Proportion of boracic acid in the unit of weight of the solution. β.	Temperature at which the deviations were observed.	Temperature at which the densities were determined.	Specific densities of the solutions corrected for the dilatation of the water. δ.	Specific rotatory power of tartaric acid on the red ray, calculated for a thickness of 100mm. $\frac{\alpha}{l\iota\delta}$. Calculated by the hyperbola.	Observed.	Excess of the power calculated by the hyperbola over that obtained by direct observation.	
1835	0·166631	0·833369	1·000000	5·0013	0·0000000	Not noticed.	+21°·0	1·07597	10°·3336	10°·9127	−0°·5791	
1835	0·166331	0·832001	0·998332	5·0021	0·00166738	...	17·0	1·07766	12·7384	12·7384	0·0000	Given by hyp.
1835	0·166063	0·830636	0·996699	5·0019	0·00330089	...	17·0	1·07813	14·8876	14·4887	+0·3989	
1835	0·165735	0·829399	0·995134	5·0048	0·00486665	...	22·5	1·07587	16·7792	16·7197	+0·0595	
1835	0·165908	0·829152	0·995060	5·0000	0·00493935	...	17·0	1·07859	16·8634	16·2276	+0·6358	
1836	0·1650926	0·8254078	0·9904996	4·9997	0·0094997	22°·0	20·0	1·07809	21·5849	21·6176	−0·0327	
1835	0·164298	0·821759	0·986057	5·0016	0·0139410	...	18·5	1·08118	25·3252	25·0926	+0·2326	
1835	0·163722	0·820239	0·983961	5·0099	0·0160383	...	22·5	1·07866	26·8621	26·6703	+0·1918	
1835	0·1620685	0·810672	0·9727405	5·0020	0·0272591	...	21·4	1·08333	33·3060	33·3060	0·0000	Given by hyp.
1836	0·1612379	0·8067532	0·9679911	5·0035	0·0320083	21°·0	20·0	1·08529	35·3766	36·4954	−0·5269	
1835	0·1610626	0·806874	0·9679366	5·0097	0·0320632	...	22·5	1·08127	35·3988	35·3154	+0·0834	
1836	0·1609742	0·8054326	0·9664068	5·0035	0·0335931	21°·5	20·0	1·08538	36·0030	36·5225	−0·5194	
1835	0·159639	0·799209	0·958848	5·0066	0·0411517	...	21·0	1·08754	38·6290	38·3159	+0·3131	
1836	0·1589643	0·7956849	0·9546492	5·0054	0·0453498	21°·0	20·0	1·08940	39·8722	39·8488	+0·0234	
1835	0·157807	0·789626	0·947433	5·0037	0·0525675	...	21·0	1·09119	41·7266	41·8894	−0·1628	
1835	0·155142	0·775310	0·930452	4·9974	0·0695477	21°·4	18·5	1·09595	45·0790	45·0790	0·0000	Given by hyp.

Equation of the hyperbola $\frac{\alpha}{l\iota\delta} = 10°·33362 + \frac{51°·88556\,\beta}{\beta + 0·034308553}$.

Obs.—The temperature at which each solution was observed always differed but very slightly from that at which the density had been determined.

Sum of the eight positive deviations.....	+1·9385
Sum of the five negative deviations	−1·8209
Total sum of the deviations	+0·1176
Mean deviation $\frac{1}{13}$.	+0·00735 Imperceptible.

Article XIII.

Photometrical Method of estimating the Intensity of ordinary and extraordinary Rays, as also those of reflected light; with Remarks on M. Cauchy's *increase in the Intensity of Light by total reflexion, and reproduction of* Fresnel's *formula for total reflexion, &c.** *By* F. E. Neumann.

[From Poggendorff's *Annalen*, vol. xl. No. 4, 1837.]

Arago's photometrical process essentially consists in the formation of a system of fringes by interference of each of the two rays, the intensity of which is to be ascertained; these two systems of fringes are allowed to fall upon one another in such a manner that the maxima of the one covers the minima of the other; one of the systems is now diminished by a *known* method, until both the systems of fringes are completely destroyed. This process is capable of almost universal application, if we allow that the law according to which the light impinging upon a perfectly transparent medium, is divided into reflected and refracted light, and when the refracting medium is a crystal, that the manner in which light is divided between the ordinary and extraordinary ray is accurately known. The knowledge of this law forms the practical foundation of M. Arago's general photometric method of proceeding, at least as far as we can ascertain from the imperfect notices which have been published of it. It will therefore not be uninteresting to give a process which allows us to estimate by observation the intensity of the reflected, refracted, ordinary and extraordinary rays with great accuracy. The principle of this process has not hitherto been applied to photometric purposes, but where the circumstances permit of its application, it has more advantages than any other with which we are acquainted. It consists in allowing the rays, whose intensity we wish to ascertain, to act upon one another. We are acquainted with two reciprocal actions of luminous rays. Two rays arising from the same source, polarized in different azimuths, and proceeding in the same direction, produce a resulting condition of the plane of polarization, the azimuth of

* Translated by Dr. J. W. Griffith. We are indebted to Sir D. Brewster for suggesting and revising the translation of this Memoir.—Ed.

which depends upon the relative intensities of the two beams. A measurement of the angle, or the azimuth of the resulting plane of polarization, thus enables us to estimate the relative intensity of the two rays. A second kind of reciprocal action of two rays of light consists in their interference, which is applied to photometric purposes in such a manner, that one ray is kept half an undulation behind the other, and this is diminished in intensity by the usual method until it completely destroys the other, whereby the equality of the two rays is very accurately ascertained, and hence, as the proportion in which one ray is diminished comparatively to the other is known, the original relation of their intensities may be deduced.

A ray of polarized light is allowed to fall upon a perfectly transparent medium; this I decompose into two others, one of which is polarized in a direction parallel to the plane of incidence, the other perpendicular to it; their amplitudes may be S and P. In this case the reflected and refracted light are likewise polarized, and the amplitudes of the former in the two component beams, which are polarized in directions parallel and perpendicular to the plane of incidence, may be R_s and R_p, but in the refracted light the intensities of the two component rays will be D_s^2 and D_p^2. Supposing the medium to be completely transparent, we obtain the following proportion for the amplitudes S, P, R_s:

$$S^2 + P^2 = R_s^2 + R_p^2 + D_s^2 + D_p^2.$$

Experiment has however shown, that R_s and D_s disappear at the same time as S, and that the same occurs with P and R_p, D_p, hence this proportion resolves itself into two others,

$$S^2 = R_s^2 + D_s^2$$
$$P^2 = R_p^2 + D_p^2.$$

These two equations would be sufficient for ascertaining the four unknown quantities R_s, R_p, D_s, D_p, if the proportions of any two were known, as $R_s : R_p$ or $D_s : D_p$. This proportion however is obtained by observing the angle formed by the plane of polarization of the reflected and refracted light with the plane of incidence. Brewster made so many observations of this angle as to enable him to deduce the following two laws:

$$\frac{R_p}{R_s} = \frac{\cos(\phi + \phi')\,P}{\cos(\phi - \phi')\,S}; \quad \frac{D_p}{D_s} = \frac{1}{\cos(\phi - \phi')}\,\frac{P}{S},$$

in these ϕ represents the angle of incidence, and ϕ' the angle of refraction. These, transferred to the above equations, give

$$P^2 = R_p^2 + D_p^2$$

$$P^2 = \left(\frac{\cos(\phi - \phi')}{\cos(\phi + \phi')}\right)^2 R_p^2 + \cos^2(\phi - \phi')\, D_p^2.$$

From these we obtain—

$$R_p^2 = P^2 \left(\frac{\tan(\phi - \phi')}{\tan(\phi + \phi')}\right)^2 D_p^2 = \frac{\sin 2\phi \sin 2\phi'}{\cos^2(\phi - \phi'), \sin^2(\phi + \phi')} P^2$$

$$R_s^2 = S^2 \left(\frac{\sin(\phi - \phi')}{\sin(\phi + \phi')}\right)^2 D_s^2 = \frac{\sin 2\phi \sin 2\phi'}{\sin^2(\phi + \phi')} S^2.$$

Fresnel's formulæ are thus proved completely and alone from observation. The same considerations apply to the posterior surface of a transparent medium; moreover, Brewster* from his experiments has deduced the same expression for $\frac{R_p}{R_s}$ and $\frac{D_p}{D_s}$ as for the anterior surface, whence R_s^2, R_p^2, D_s^2, D_p^2 have the same value as at the anterior surface.

M. Cauchy has deduced formulæ for the intensity of the refracted and reflected light at the surfaces of two media, from his new principles†. In his second letter, addressed to M. Libri‡, he has given the following formulæ for the refracted light, using the same signs:

$$D_p^2 = \frac{4 \sin^2 \phi' \cos^2 \phi}{\sin^2(\phi + \phi') \cos^2(\phi - \phi')} P^2, \quad D_s^2 = \frac{4 \sin^2 \phi' \cos^2 \phi}{\sin^2(\phi + \psi')} S^2 \quad (a.)$$

M. Cauchy draws a conclusion from these formulæ which must have greatly astonished philosophers, *i. e.* that at the moment at which total reflexion occurs, and when, consequently, the reflected light possesses the same intensity as the incident, the transmitted ray, instead of disappearing, becomes much increased in intensity. In fact this result is at once evident. If $\sin \phi' = 1$, and consequently $\sin \phi = \frac{1}{m}$, m expressing the coefficient of refraction, we obtain from (*a.*),

$$D_p^2 = 4 m^2 P^2, \quad D_s^2 = 4 S^2,$$

whence the transmitted ray would be $4 m^2$, or four times as great as the incident, according as it has become polarized perpendicular, or parallel to the plane of incidence; for ordinary light, the increase would be $2 (m^2 + 1)$, *i. e.* when glass is used

* Phil. Trans., Part I., 1830, p. 145.
† *Mémoire sur la Dispersion*, &c. p. 203.
‡ *Comptes Rendus*, 1836, 1ier Sem. p. 427.

about 6·5 times. M. Cauchy in these remarkable results refers to experiments which he instituted with M. Hessler of Grätz, which however merely showed "that the escaping ray gradually disappeared as the incident ray was caused to make a less and less angle." I have in vain endeavoured to observe any increase in the intensity of the escaping ray at the instant of total reflexion.

The disagreement of M. Cauchy's formula (*a.*) with that of Fresnel is alone sufficient to show that it is opposed to experiment. M. Cauchy has assumed the square of the magnitudes of the refracted ray and incident light as the proportion of intensities, instead of the proportion of their actual power. Consequently, if D_p^2 and D_s^2 in M. Cauchy's formula expresses the intensity of the refracted light, its value must be multiplied by some factor, which expresses the relation of the mass, which is set in motion by the same undulation in the incident and refracted light. The introduction of this factor gives the correction of the formula (*a.*). I find it by dividing Fresnel's formula by M. Cauchy's,

$$\frac{\cos\phi'}{\sin\phi'} \cdot \frac{\sin\phi}{\cos\phi}.$$

Hence it is seen that the new principle from which M. Cauchy has deduced his formula, is essentially based on the supposition that the luminiferous æther possesses the same elasticity in different media, and that the refraction of the light is produced by its varying density alone. This is Fresnel's hypothesis. Its inadequacy, or rather inadmissibility, in crystalline substances, induced me to give it up, and to regard the refraction of light as produced by the difference in elasticity alone, as may be seen in my treatise published in the Transactions of the Berlin Academy, "On the Influence of the surfaces of Crystals on reflected Light, and the Intensity of the ordinary and extraordinary Ray." I return to the main object of this communication, *i. e.* to detail the methods which I adopt for ascertaining experimentally the distribution of light falling upon the surface of a transparent crystalline medium, between the reflected, the ordinary, and the extraordinary rays.

Suppose the incident light, the intensity of which is P^2, to be polarized at right angles to the plane of polarization. The reflected light is also polarized, but there is no ground for supposing that it is polarized at right angles to the plane of incidence; experiment shows the contrary; thus I decompose it into one

which is polarized at right angles to the plane of incidence, and one which is polarized in a plane parallel to it, expressing the intensity of the former by $p^2\,P^2$, and of the latter by $p'^2\,P^2$. I call the intensity of the ordinary ray $\omega'^2\,P^2$, and that of the extraordinary $\omega''^2\,P^2$. When the incident light is polarized in a plane parallel to that of incidence, I call its intensity S^2. The intensity of that component of reflected light which is polarized parallel to the plane of incidence, would be $s^2\,S^2$; that polarized perpendicularly would be $s'^2\,S^2$, and the intensities of the ordinary and extraordinary rays would be $\sigma'^2\,S^2$ and $\sigma''^2\,S^2$. We are now in a condition to express the intensity of the reflected and refracted light, when the incident ray is polarized in any azimuth. P^2 and S^2 would represent the intensities of the component rays of the incident light, $R_p{}^2$ and $R_s{}^2$ those of the reflected ray, and those of the ordinary and extraordinary ray would be D'^2 and D''^2. The ray $R_p{}^2$ is composed of $p^2\,P^2$ and $s'^2\,S^2$; these are two rays having the same origin polarized in the same direction; they form a compound ray the intensity of which is $(p\,P+s'\,S)^2$. The ray $R_s{}^2$ is likewise composed of the rays $p'^2\,P^2$ and $s^2\,S^2$, its intensity is consequently $(p'\,P+s\,S)^2$. The same applies to D' and D''. We thus have

$$\begin{aligned} R_p &= p\;P+s'\;S,\\ R_s &= p'\;P+s\;\;S,\\ D' &= \omega'\,P+\sigma'\,S,\\ D'' &= \omega''\,P+\sigma''\,S. \end{aligned}$$

In consequence of the assumed perfect transparency of the medium, we have

$$P^2+S^2=R_p{}^2+R_s{}^2+D'^2+D''^2.$$

This equation must apply, whatever the values of P and S, which are independent of one another, may be. If for R_p, R_s, D' and D'', we substitute their values, the equation resolves itself into the following three formulæ:—

$$\begin{aligned} 1 &= p^2 + p'^2 + \omega'^2 + \omega''^2,\\ 1 &= s'^2 + s^2 + \sigma'^2 + \sigma''^2,\\ 0 &= p\,s'+p's+\omega'\sigma'+\omega''\sigma''. \end{aligned}$$

One of the two rays composing the ordinary ray may be expressed as half an undulation behind the other, by a proper arrangement of P and S, *i. e.* by the proper arrangement of the azimuth of polarization of the incident ray; then each ray will diminish the intensity of the other, and at a certain value of $-\frac{P}{S}$ they will completely destroy one another; this value of $-\frac{P}{S}$

is equal to the value of $\frac{\sigma'}{\omega'}$. We thus ascertain the proportion $\frac{\sigma'}{\omega'}$, and likewise $\frac{\sigma''}{\omega''}$, by observing the azimuth of polarization of the incident ray, at which the ordinary and extraordinary ray disappear. If we observe the original azimuth of polarization, at which all reflected light is polarized in the plane of incidence, consequently where $R_p = p\,P + s'\,S = 0$, we obtain $\frac{s'}{p}$; if we observe the azimuth of polarization of the reflected ray, when the incident ray is polarized in a direction parallel to the plane of incidence, where $R_p = s'\,S$ and $R_s = s\,S$, we have in the tangent of this azimuth the value of $\frac{s'}{s}$, &c. In general when a is the azimuth of polarization of the incident ray, $\tan a = \frac{P}{S}$, and α that of the reflected ray, we have

$$\tan \alpha = \frac{p \tan a + s'}{p' \tan a + s}.$$

If we gradually give a different values, and observe each time the α belonging to it, we obtain as many equations, from which the proportion of the magnitudes p, p', s, s' can be ascertained with great accuracy. Thus three only of the unknown magnitudes p, p', s . . . . . remain unestimated, and these are obtained from the three equations which the supposition of the transparency has yielded.

I will illustrate this by an example, based upon observations, which I made of the natural surface of cleavage of calcareous spar.

The light was incident at about 45°, and the plane of incidence was perpendicular to the surface of the section. I must first explain what I mean by positive and negative azimuth of the plane of polarization. I suppose the feet to face the crystal, the incident plane of vibration being directed forwards, and when the plane of polarization is now on my *left*-hand I call its azimuth *positive*; when the plane of polarization is on my right, negative. The same consideration applies to the reflected plane of vibration, where I again suppose myself lying in it and moving forwards, the feet facing the reflecting surface. The azimuth of the plane of incidence, formed from the surface of the section, I call plus, when supposing myself standing on the surface of the crystal, my

face having its axis directed towards the point of section, the plane of incidence lies on my right-hand. This being determined, my observations are as follows; a indicating the azimuth of polarization of the incident beam, and α that of the reflected.

Incidence 45°, azimuth of the plane of incidence +90.

1. The extraordinary ray disappeared when a was $= -65° 25'$.
2. The ordinary ray disappeared when a was $= +22° 28'$.
3. when $a = 0$, α was $= -2° 24'$.
4. „ $a = 90$, α „ $= +84° 3'$.
5. „ $\alpha = 0$, a „ $= -6° 19'$.
6. „ $\alpha = 90$, a „ $= 87° 23'$.
7. „ $\alpha = +83° 55'$, a „ $= +89° 57'{\cdot}5$.
8. „ $\alpha = +20° 29'$, a „ $= -46° 30'$.
9. „ $\alpha = -32° 39'$, a „ $= +53° 33'$.
10. „ $\alpha = -45°$, a „ $= +64° 19'$.
11. „ $\alpha = +45°$, a „ $= -70° 23'$.

We thus obtain the following equations:—

1. $-\omega'' \tan 65° 25' + \sigma'' = 0.$
2. $\omega' \tan 22° 28' + \sigma' = 0.$
3. $-\tan 2° 24' = \frac{s'}{s}.$
4. $\tan 84° 3' = \frac{p}{p'}.$
5. $-p \tan 6° 19' + s' = 0.$
6. $p' \tan 87° 23' + s = 0.$
7. $\tan 83° 55' = \frac{p \tan 89° 57'{\cdot}5 + s'}{p' \tan 89° 57'{\cdot}5 + s}.$
8. $\tan 20° 29' = \frac{-p \tan 46° 30' + s'}{-p' \tan 46° 30' + s}.$
9. $-\tan 32° 39' = \frac{p \tan 53° 33' + s'}{p' \tan 53° 33' + s}.$
10. $-\tan 45° = \frac{p \tan 64° 19' + s'}{p' \tan 64° 19' + s}.$
11. $\tan 45° = \frac{-p \tan 70° 23' + s'}{-p' \tan 70° 23' + s}.$

I find from these 11 equations,

$$\omega' = -\sigma' \cot 22° 28', \text{ and } p = -s \tan 22° 30'.$$
$$\omega'' = +\sigma'' \cot 65° 25', \text{ and } p' = -s \tan 2° 32'.$$
$$s' = -s \tan 2° 31'.$$

Thus the equations, on account of the complete transparency, become—

$$1=[\tan^2 22^\circ 30' + \tan^2 2^\circ 32']s^2 + \sigma'^2 \tan^2 67^\circ 32' + \sigma''^2 \tan^2 24^\circ 35'.$$

$$1=[1+\tan^2 2^\circ 31']s^2 + \sigma'^2 + \sigma''^2.$$

$$0=[\tan 22^\circ 30' . \tan 2^\circ 31' - \tan 2^\circ 32']s^2 - \sigma'^2 \tan 67^\circ 32'. + \sigma''^2 \tan 24^\circ 35'.$$

Hence	$s^2=0{\cdot}1078.$	$\sigma'^2=0{\cdot}1409.$
	$p^2=0{\cdot}01850.$	$w'^2=0{\cdot}8241.$
	$s'^2=0{\cdot}000207.$	$\sigma''^2=0{\cdot}7510.$
	$p'^2=0{\cdot}000212.$	$w''^2=0{\cdot}1572.$

By means of these values we now find the intensity of the reflected ray and that of the two refracted ones, in whatever azimuth the incident ray is polarized; thus we have only to substitute these values in the expressions for R_p, R_s, D', D''. If the incident light is common and its intensity $=1$, the intensity of the reflected ray is $\frac{s^2+p^2+s'^2+p'^2}{2} = 0{\cdot}0633$; that of the ordinary is 0·4825; of the extraordinary 0·4541. In my treatise which I just now alluded to, I have calculated these three intensities and find them 0·0632 for the reflected light, 0·4825 for the ordinary ray, and 0·4542 for the extraordinary ray; so that they agree almost perfectly to the fourth decimal place. An accurate discussion of the errors which can possibly occur in the final result would show that, by this method of estimating the intensity, the quantities of reflected and refracted light may be accurately calculated even to $\frac{1}{1000}$th of that incident.

In a third letter* to M. Ampère, M. Cauchy has reproduced Fresnel's formula for total reflexion from his new principles. The principles of my theory, applied to this case, give the same expressions. I was first led to its application from an observation in M. Cauchy's paper on the use of experimental magnitudes instead of the imaginary sines and cosines, hence they are not used in my treatise, but I will take the opportunity of communicating them here. The differential equations, upon which the movements of the æther in an uncrystalline transparent medium depend, when the plane of vibration is parallel to the coordinate axis z, and u, v, w express the movements of the particles parallel to the axis x, y, z, are,—

* *Comptes Rendus*, 1ier Sem. 1836, p. 364.

$$\left.\begin{aligned}\frac{1}{a}\frac{d^2u}{dt^2} &= \frac{3\,d^2u}{dx^2} + \frac{d^2u}{dy^2} + \frac{2\,d^2v}{dx\,dy}\\ \frac{1}{a}\frac{d^2v}{dt^2} &= \frac{d^2v}{dx^2} + \frac{3\,d^2v}{dy^2} + \frac{2\,d^2u}{dx\,dy}\\ \frac{1}{a}\frac{d^2w}{dt^2} &= \frac{d^2w}{dx^2} + \frac{d^2w}{dy^2}.\end{aligned}\right\} \quad . \quad . \quad . \quad (1.)$$

We can remove the third plane of vibration moving perpendicularly to its plane, from the two first equations, by introducing the condition—

$$\frac{du}{dx} + \frac{dv}{dy} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

whereby they become changed to—

$$\left.\begin{aligned}\frac{1}{a}\frac{d^2u}{dt^2} &= \frac{d^2u}{dx^2} + \frac{d^2u}{dy^2}\\ \frac{1}{a}\frac{d^2v}{dt^2} &= \frac{d^2v}{dx^2} + \frac{d^2v}{dy^2}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

A special integral of the equations (3.) which satisfies the condition (2.), exists when the plane of vibration forms the angle ϕ with the axis y:

$$\left.\begin{aligned}u &= -\,A\sin\phi\sin\left(\frac{x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)2\pi\\ v &= \quad A\cos\phi\sin\left(\frac{x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)2\pi,\end{aligned}\right\} \quad . \quad (4.)$$

in which $a\,T^2 = \lambda^2$, λ expressing the length of the undulations, and T their duration. From the third equation in (1.) we obtain

$$w = C\sin\left(\frac{x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)2\pi. \quad . \quad . \quad . \quad (5.)$$

These special integrals are sufficient to allow of the deduction of the laws of reflexion and refraction. Thus, if we suppose the medium to border closely upon a second in the plane of y and z, a reflected and transmitted vibration exists at this border. The reflected vibration must require the same differential equations as the incident, it is also parallel with the axis z, but forms the angle $180 - \phi$ with y, hence, when its vibrations are expressed by u', v', and w',

$$\left.\begin{aligned}u' &= A'\sin\phi\sin\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)2\pi\\ v' &= A'\cos\phi\sin\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)2\pi\\ w' &= \quad C'\sin\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)2\pi\end{aligned}\right\} \quad (6.)$$

in which A′ and C′ form new constants. The refracted vibration must satisfy the differential equations of the second medium, which differ from those in (1.) in the value of a, which I shall call a'; it is parallel with z and forms the angle ϕ' with y. If we express its vibrations by u'', v'' and w'', and call $\lambda'^2 = a'\,T^2$ the length of its undulations, we have

$$\left.\begin{aligned} u'' &= -\,A''\sin\phi'\sin\left(\frac{x\cos\phi' + y\sin\phi}{\lambda'} - \frac{t}{T}\right)2\pi \\ v'' &= A''\cos\phi'\sin\left(\frac{x\cos\phi' + y\sin y'}{\lambda'} - \frac{t}{T}\right)2\pi \\ w'' &= \quad C''\sin\left(\frac{x\cos\phi' + y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi. \end{aligned}\right\} \quad (7.)$$

A′, C′ and A″, C″, i. e. the amplitudes of the reflected and refracted waves, are estimated from the amplitudes of the incident waves A and C. Thus, my principles are,—1, that the motions which the particles experience at the borders of the two media, i. e. $x = 0$, are similar to the two waves of the first medium in direction and in the amplitude of the motions which they obtain from the waves of the second medium; 2nd, that the active power of the incident waves is equal to the sum of the active powers in the reflected and refracted waves; 3rd, that the æther possesses the same density in both media. Now the quadratic equation between the magnitudes A, A′, A″, C, C′, C″, which the principle of obtaining the active forces yields, may always be replaced by a linear one, as shown by calculation, and in uncrystalline media, it is this which expresses that the pressure on the refracting surface, which takes place from the dislocation of the portions in the first medium, contains the same component perpendicular to the plane of incidence, but the pressure which is produced by the dislocation in the second medium, *i. e.* the equation of the active force, may here be replaced by

$$\left.\begin{aligned} & a\frac{dw}{dx} + a\frac{dw'}{dx} = a'\frac{dw''}{dx} \\ \text{or because} \quad & \frac{a'}{a} = \frac{\sin^2\phi'}{\sin^2\phi}, \text{ by} \\ & \frac{dw}{dx}\sin^2\phi + \frac{dw'}{dx}\sin^2\phi = \frac{dw''}{dx}\sin^2\phi'. \end{aligned}\right\} \quad (8.)$$

We thus immediately ascertain the motion from the equality of the components:

$$\left.\begin{aligned} +(A-A')\sin\phi &= +A''\sin\phi \\ (A+A')\cos\phi &= A''\cos\phi' \\ C+C' &= C'' \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (9.)$$

and on account of the equality of the components of the pressure on the refracting plane being perpendicular to the plane of incidence,

$$(C-C')\frac{\sin^2\phi\cos\phi}{\lambda} = \frac{C''\sin^2\phi'\cos\phi'}{\lambda'}$$

or as

$$\frac{\sin\phi}{\lambda} = \frac{\sin\phi'}{\lambda'}.$$

$$(C-C')\sin\phi\cos\phi = C''\sin\phi'\cos\phi. \quad . \quad . \quad (10.)$$

The solution of the equations (9.) and (10.) reproduces Fresnel's expression for the reflected and refracted magnitudes, supposing that the plane of polarization be allowed to pass through the ray and the direction of its vibrations. However, when a ray enters a lower refractive medium from a higher, and has passed beyond the limits of total reflection, *i. e.* when $\sin\phi' > 1$, $\cos\phi'$ is imaginary. According to M. Cauchy's observation, we must in this case substitute exponential magnitudes for $\sin\left(x\frac{\cos\phi}{\lambda}\right)$ and $\cos\left(x\frac{\cos\phi}{\lambda}\right)$. We can satisfy the differential equations (3. and the third in 1.) by

$$\left.\begin{aligned} u'' &= \sin\phi' e^{\frac{-x\sqrt{-1}\cos\phi'}{\lambda'}} \\ &\quad + \left\{A''\sin\left(\frac{y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi + B''\cos\left(\frac{y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi\right\} \\ v'' &= \sqrt{-1}\cos\phi' e^{\frac{-x\sqrt{-1}\cos\phi'}{\lambda'}} \\ &\quad \times \left\{B''\sin\left(\frac{y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi - A''\cos\left(\frac{y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi\right\} \\ w'' &= e^{\frac{-x\sqrt{-1}\cos\phi'}{\lambda'}} \\ &\quad \times \left\{C''\sin\left(\frac{y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi + D''\cos\left(\frac{y\sin\phi'}{\lambda'} - \frac{t}{T}\right)2\pi\right\}. \end{aligned}\right\} \quad (11.)$$

Moreover, we know that in reflected light the component rays suffer a certain retardation, consequently we must add a member to the equations (6.) in $\cos\left(\frac{x\sin\phi + y\sin\phi}{\lambda} - \frac{t}{T}\right)$, so that

$$\left.\begin{aligned}
u' &= \mathrm{A}' \sin\phi \sin\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
&\quad + \mathrm{B}' \sin\phi \cos\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
v' &= \mathrm{A}' \cos\phi \sin\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
&\quad + \mathrm{B}' \cos\phi \left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
w' &= \mathrm{C}' \sin\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
&\quad + \mathrm{D}' \cos\left(\frac{-x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi.
\end{aligned}\right\} \quad (12.)$$

The equations for the incident light remain unaltered; thus

$$\left.\begin{aligned}
u &= -\mathrm{A}\sin\phi \sin\left(\frac{x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
v &= \mathrm{A}\cos\phi \sin\left(\frac{x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi \\
w &= \mathrm{C}\sin\left(\frac{x\cos\phi + y\sin\phi}{\lambda} - \frac{t}{\mathrm{T}}\right) 2\pi.
\end{aligned}\right\} \quad (13.)$$

The equality of the components of the motion in these three systems of waves 11, 12, and 13, x being $= 0$, give

$$\left.\begin{aligned}
\mathrm{A}\sin\phi - \mathrm{A}'\sin\phi &= -\mathrm{A}''\sin\phi' \\
\mathrm{B}'\sin\phi &= +\mathrm{B}''\sin\phi' \\
\mathrm{A}\cos\phi \quad \mathrm{A}'\cos\phi &= \quad \mathrm{B}''\sqrt{-1}\cos\phi' \\
\mathrm{B}'\cos\phi &= -\mathrm{A}''\sqrt{-1}\cos\phi'.
\end{aligned}\right\} \quad (a.)$$

$$\left.\begin{aligned}
\mathrm{C} + \mathrm{C}' &= \mathrm{C}'' \\
\mathrm{D}' &= \mathrm{D}'',
\end{aligned}\right\} \quad (b.)$$

and the equation (8.), applied to 11, 12, and 13, gives—

$$\left.\begin{aligned}
(\mathrm{C} - \mathrm{C}')\sin\phi\cos\phi &= -\mathrm{D}''\sqrt{-1}\sin\phi'\cos\phi' \\
\mathrm{D}'\sin\phi\cos\phi &= -\mathrm{C}''\sqrt{-1}\sin\phi'\cos\phi'.
\end{aligned}\right\} \quad (c.)$$

Consequently we see, from the equations (a.), that

$$\mathrm{A}^2 = \mathrm{A}'^2 + \mathrm{B}'^2,$$

and from b and c, that

$$\mathrm{C}'^2 = \mathrm{C}'^2 + \mathrm{D}'^2,$$

i. e. that all the light is reflected. Moreover, we obtain from a,

$$A' = \frac{\sin^2\phi\,(\sin^2\phi' - 1) - \cos^2\phi\sin^2\phi'}{\sin^2\phi\,(\sin^2\phi' - 1) + \cos^2\phi\sin^2\phi'}\,A$$

$$B' = \frac{2\sin\phi\cos\phi\sin\phi'\sqrt{\sin^2\phi' - 1}}{\sin^2\phi\,(\sin^2\phi' - 1) + \cos^2\phi\sin^2\phi'}\,A;$$

and from b and c,

$$C' = \frac{\sin^2\phi\cos^2\phi - \sin^2\phi'(\sin^2\phi' - 1)}{\sin^2\phi\cos^2\phi + \sin^2\phi'(\sin^2\phi' - 1)}\,C$$

$$D' = \frac{2\sin\phi\cos\phi\sin\phi'\sqrt{\sin^2\phi' - 1}}{\sin^2\phi\cos^2\phi + \sin^2\phi'(\sin^2\phi' - 1)}\,C,$$

which are exactly Fresnel's formulæ, from which he deduced the difference in the retardation of the two component rays polarized at right angles to one another on total reflexion, and thus the laws of elliptical polarization resulting from this*.

* *Ann. de Chim. et de Phys.* t. xlvi. p. 225.

Article XIV.

On the Nature of Aqua Regia, *on Hyponitric Acid as an oxidizing agent, on the Constitution of that Acid, and the part which it acts towards Organic Substances. By* Dr. Kœne, *Professor of Chemistry in Brussels*.*

[From Poggendorff's *Annalen der Physik und Chemie*, 1845, No. 3.]

1. AMONG the most powerful agents for oxidizing, acidifying or dissolving a large number of simple and compound bodies, *aqua regia* occupies the first place. Nevertheless this liquid, so important for the above purposes and so interesting on account of the phænomena which accompany them, is one of those whose nature is but very imperfectly known.

2. Berthollet ascribes the properties of *aqua regia* to the formation of chlorine and nitrous acid.

3. This view was adopted by Sir Humphry Davy, who obtained a liquid by the addition of hydrochloric acid to nitrous acid, which did not possess the properties of *aqua regia*. But at the time when Davy made this experiment the hyponitric acid was not yet known. The English chemist may therefore have very possibly worked with this acid, since several French chemists, following M. Dumas, look upon it as a compound radical, and as a less powerful oxidizing agent than nitric acid, and capable of replacing hydrogen in some organic substances which contain more than 1 equivalent of that metalloid.

4. Lastly, M. Millon considers the nitrous acid to be the most powerful oxidizing agent of the different oxides of nitrogen, an hypothesis which leads to the assumption that the hydrogen of the hydrochloric acid is capable of destroying the nitrous acid, since the same metalloid deoxidizes nitric acid.

5. The point then to be ascertained, is whether hydrochloric acid reduces nitric acid to hyponitric acid, to nitrous acid, or to nitric oxide.

6. If it were decidedly proved that nitrous acid was the most powerful oxidizing agent of the three oxyacids of nitrogen, the last hypothesis might deserve the preference. But if we bear in

* Translated by W. Francis, Ph. D., F.L.S.

mind the observations made by Davy (3.), and take into consideration the oxidizing power of hyponitric acid, the formation of which in the action of nitric oxide on nitric acid precedes that of the nitrous acid, we come to the conclusion that hydrochloric acid is capable of reducing nitric only to nitrous acid.

7. However, the constitution of the oxy-sulpho-sulphuric acid and analogous acids, the hypothesis which regards the hyponitric acid as a radical, and the formation of hydrochloric acid and nitric acid on the addition of water to a solution of chlorine in hyponitric acid, lead rather to the view that *aqua regia* is the result of a *mutual reaction* between the elements of the hydracid and those of the oxy-acid,

$$(H + Cl) + (NO^4 + O)(H + O) + (NO^4 + Cl),$$

in accordance with which therefore water and oxy-chloro-nitric acid are formed, which last is not permanent, but like the analogous acids, possesses the property of being decomposed by water.

Since the last hypothesis was preferred to the two others (2. 4.), it was determined to allow an excess of gaseous hydrochloric acid to act upon concentrated nitric acid. But as in the reaction between these acids water is formed, and this liquid, whose quantity continually increases, prevents the complete decomposition of the acids, it was important for the quantitative determination of the hydrochloric acid, whose elements combine with those of the nitric acid, that the acids should be allowed to act on one another, protected from the influence of the water, *i. e.* in the presence of a liquid which would combine with the water, as it was formed without this hygroscopic fluid having sufficient influence on the products of the reaction to prevent the latter from being completed.

8. Sulphuric acid satisfies these conditions. This compound moreover possesses, *when it is present in great excess*, the property of retaining the hyponitric and nitrous acids in solution at the temperature of the elimination of the chlorine, a property which is absolutely requisite for the decision of the question; because an excess of hydrochloric acid must be used to destroy the whole of the nitric acid employed, and it is consequently necessary to determine the amount of this excess.

9. This determination requires that we should be able to protect ourselves from the influence of the chlorine, the liberated quantity of which cannot be determined under these circumstances, because before the free chlorine has been expelled by

heat from its solution in sulphuric acid, red vapours begin to be disengaged. These vapours would, on being passed through an aqueous solution of chlorine, again form hydrochloric and nitric acids.

10. In the present case, therefore, the hydrochloric acid must be determined according to the process which I have described in a previous communication*.

After these preliminary observations I might pass on to the description of the apparatus I employed, the processes I adopted, and to an infinity of precautionary measures I took in order to determine accurately the quantity of hydrochloric acid which escaped the action of the nitric acid, the amount of actual acid in which had been previously ascertained; but since the analyses made with various quantities of substances led to no results agreeing with the above theory, their description would be superfluous. For although it is without contradiction to be expected that in analyses of this kind very perceptible losses must occur, it is not the less true that when it is a question of a loss of more than half an equivalent of hydrochloric acid, the cause must be sought for elsewhere than in the complication of the apparatus, or of the analysis.

11. Since the cause of this might be supposed to be owing to the deoxidation which the hyponitric acid experiences under the influence of the action of the hydrochloric acid, vapours of hyponitric acid were passed into 100 grammes of pure concentrated sulphuric acid. They were prepared by heating 5 grammes of well-dried nitrate of lead. Afterwards gaseous hydrochloric acid was passed into the acid solution. It liberated a considerable quantity of chlorine from the solution of the sulphate of potash (10.).

To ascertain whether the nitrous acid had been decomposed by the hydrochloric acid, the following method was adopted.

12. A current of hydrochloric acid was passed for half an hour into a solution of 100 grammes of pure sulphuric acid, and 2·1 grammes hyponitric acid; and after the chlorine and hydrochloric acid had been expelled by heat, one-half of it was again subjected to the action of hydrochloric acid, but this time no chlorine was formed. A portion of the other half was mixed with a sixth of its volume of water, from which all air had been

* Poggendorff's *Annalen*, vol. lxiv. p. 404.

expelled. This water was poured into a flask full of carbonic acid*. Acid was now added to the water, and as soon as the vessel was filled with it, it was closed hermetically. After the cooling of the acid, a couple of drops of hydrochloric acid were added, the vessel was then closed and shaken, on opening the flask half an hour afterwards a distinct odour of chlorine was evolved.

In this experiment it is requisite,—1, to add the acid to the water, that nitric acid may be formed in the first moment of the addition; 2, to arrange it in such a manner that the flask filled with the acid mixture contain nearly 6 parts of acid to 1 of water, in order that too much water may not be present, and so the action of the hydrochloric acid on the nitric acid formed in the first moment be not prevented (7.).

13. Sulphuric acid which had been employed in the concentration of commercial nitric acid, was heated until its boiling-point remained constant. The acid, treated as above with water and hydrochloric acid, exhibited the same phænomena, but no chlorine was ever formed with hydrochloric acid alone.

14. 10 grammes of red nitric acid were added to 150 grammes of the concentrated sulphuric acid of the experiment (13.). It lost on solution its intense red colour; but on heating the acid mixture in a retort with a drawn-out neck bent at right angles, the red vapours again made their appearance. An effervescence occurred between 170° and 180° C., which arose chiefly from a disengagement of oxygen. At 190° this evolution of gas was so considerable, that the liquid appeared to boil violently; but from this temperature the formation of oxygen decreased perceptibly, and at 250° no more was disengaged. At the same time with the oxygen red nitric acid distilled over, amounting to about one-third of what had been added to the sulphuric acid.

When the temperature of the acid had reached 326°, the neck of the retort was introduced into a vessel in which carbonic acid was constantly evolved, and the flame of the spirit-lamp gradually diminished. The acid, which on boiling possessed an intense yellow colour, became perfectly colourless during the cooling.

15. When it had reached the ordinary temperature, the acid formed no chlorine with hydrochloric acid; treated previously

* Since the non-existence of the sulphate of nitric oxide had not then been shown, this precaution was necessary.

with water, as in the experiments (12, 13.), the acid yielded chlorine on the addition of some hydrochloric acid.

Another portion of the acid mixed with alcohol, access of air being prevented, formed nitric æther. Copper dissolved in it with a violet colour and with disengagement of nitric oxide.

After having adapted a funnel with a cock into the tubulure of a retort containing water, carbonic acid was first conveyed into the funnel and then 26 grammes acid. Upon this heat was applied, and when the water boiled, the cock was opened. The temperature of the water rose considerably by the addition of the acid; at the same time red vapours were evolved, which were received in water containing carbonate of lime in suspension; it was then heated until the temperature of the acid had attained the boiling-point of sulphuric acid. The liquid decanted from the carbonate of lime was evaporated to dryness and the residue exhausted with alcohol. The alcoholic liquid yielded on desiccation a residue which left on ignition 0·21 gramme lime.

Having established these facts, we will now apply them to *aqua regia* and hyponitric acid, to ascertain more precisely the nature of these liquids.

On the Nature of Aqua Regia.

16. *Aqua regia* is characterized and effective only under very special conditions. The circumstances which principally prevail at its formation, are the temperature, the degree of concentration of the two acids forming it, and the presence of a body capable of combining with the chlorine.

17. No reaction takes place in a mixture of hydrochloric and nitric acid, both concentrated, at a very low temperature; the cold liquids mix without acquiring any colour and without elimination of chlorine, but on being removed from the refrigerating mixture, to a place where the temperature is 0°, it gradually becomes coloured and disengages chlorine.

18. A mixture of 2 volumes of hydrochloric acid of 37·60 per cent. and 1 volume of red nitric acid begins to form chlorine only at − 12° C. Nitric acid of 74·5 per cent. of real acid begins with the same hydrochloric acid, to become coloured and form chlorine near about − 6° C. The presence of a larger quantity of water delays the action still more, and when the acids are very dilute, the action does not occur even on the application of heat; but if in the latter case a metal is immersed in the liquid, the effect is immediately produced and water is formed.

Soon after, water weakens the affinities to such a degree that the reaction would cease if we were not to employ a metal of the sixth division, for instance, gold.

19. These phænomena show that the formation of the *aqua regia* by no means results from a reciprocal action between the elements of the hydrochloric and nitric acids (the latter considered according to the formula $NO^4 + O$), but it originates from the action of the hydrogen of the one on the oxygen of the other. In fact, for the action to occur, it is requisite that either heat, or a body having affinity for chlorine, or both at the same time, diminish the affinity of the chlorine for the hydrogen of the hydrochloric acid, and increase that of the same chlorine for the hydrogen of the water, so that the dehydrating effect of the nitric acid is rendered more powerful.

Now if the reaction took place under the influence of a double affinity (7.) *these phænomena would not occur, the chlorine would not be disengaged or enter into a combination precisely when formed with the hyponitric acid.*

In making these observations, we have by no means left out of consideration the various circumstances in which a chemical action occurs at the very moment when the affinities which called it into existence are annihilated. We have even placed the hypothesis which considers the hyponitric acid as a radical at the head of these observations, and we have endeavoured to support it by allowing gaseous hydrochloric acid to act upon concentrated nitric acid at a low temperature, and protected from the influence of water, but instead of obtaining the compound $NO^4 + Cl$, we observed and showed that these acids are reduced to water, chlorine and nitrous acid (11, 12, 14). These then are the products which the active *aqua regia* yields. With respect to the causes from which they proceed, these may be—1, the tendency of the chlorine to assume the gaseous state, or to combine with the metal; 2, the slight stability of the nitric acid, and its dehydrating power; 3, the tendency of the nitrous acid to escape or to enter into combination*.

* M. Baudrimont states that he obtained a peculiar gas on acting with commercial hydrochloric acid upon nitric acid at a temperature of 86° C. This gas, which he regards as the active principle of *aqua regia*, would correspond to nitric acid, and be represented by the formula $NO^3 Cl^2$.

I know not whether M. Baudrimont has allowed himself to be guided by the hypothesis of E. Davy, according to which the product of nitric acid on fused chloride of sodium is the active principle of *aqua regia*; but so much is certain, that if the chlorazotic acid exists, it must possess very peculiar properties,

Hyponitric Acid considered as an Oxidizing Agent.

20. We have just seen that the action between the hydrochloric and nitric acid ceases as soon as the latter is reduced to nitrous acid. This evidently arises from the circumstance that the oxygen in the latter acid is more intimately combined than in the nitric and hyponitric acids. The nitrous acid is consequently the most stable, and therefore the least oxidizing of the three oxy-acids of nitrogen.

This conclusion, deduced from the reactions to which hydrochloric, nitric and hyponitric acids give rise in concentrated sulphuric acid, is widely different from that which M. Millon has drawn from his experiments. According to this chemist, the general course in oxidations by means of nitric acid is, that the nitrous acid which first originates forms nitrite of copper, mercury, silver, &c., that these are destroyed as they are formed, and that this destruction gives rise to the production of nitric oxide, which again forms nitrous acid with the nitric acid present, whence proceeds a fresh action and a fresh destruction*.

21. We are not aware whether, in the action of a metal upon nitric acid, the formation of nitrite always precedes that of nitrate; however, it appears to me that the origin of a nitrite by the action of an alkali on a saturated solution of nitric oxide in nitric acid does not admit of our adopting the hypothesis of M. Millon†, because the formation of the hyponitric acid precedes that of the nitrous acid, and because, when the nitric acid is present, as is usually the case, in excess, only hyponitric acid is formed. Nor can we conceive how nitrous acid, considered as one of the most powerful oxidizing agents, could combine with protoxide of mercury.

The existence of the protonitrate of mercury, the circum-

among others, that of parting with nitrous acid to sulphuric acid (see the details of my experiments), *of not combining with the elements of water*, but yielding with the metalloids, nitrates and chlorides; acting upon gold, and producing an explosion with pulverulent silver, *but only acting slowly upon potassium*, producing an intense evolution of heat and light with powdered antimony or arsenic, *without giving rise to the same phænomena with fused phosphorus.—Annal. der Chem. und Pharm.*, vol. xlviii. p. 202, and *Traité de Chimie générale*, par A. Baudrimont, vol. i. p. 616.

If the French chemist, instead of using the crude products of commerce, had worked with dry hydrochloric acid and monohydrated nitric acid; if, moreover, he had dried the chlorazotic gas, and had assured himself of the absence of hydrochloric acid, we should be in a condition to judge of the value of an investigation the statements of which require a most minute study.

* *Comptes Rendus*, vol. xiv. p. 912. † *Ibid*, p. 911.

stances attending its formation, the property possessed by phosphorous acid of resisting the oxidizing action of nitrous acid*, the formation of nitrous acid by the action of hydrochloric acid upon nitric and hyponitric acids, that of the hyponitric acid by the action of nitric oxide upon an excess of nitric acid, the circumstances attending the formation of the nitrite of the oxide of ethyle, and the influence of heat on the alkaline nitrates,—all these facts are irreconcileable with the hypothesis of M. Millon; and the most important observations made by the author himself, prove most evidently that of all the oxides of nitrogen the hyponitric acid is the most powerful oxidizing agent†.

Were it otherwise, if the hyponitric acid were a less powerful oxidizing agent than nitrous acid, there would be an anomaly in the oxidizing properties of these oxides, which constitute the more powerful oxidizing agent the more oxygen they contain. Thus nitric oxide, which is converted in the presence of iron, zinc, or phosphuretted hydrogen into protoxide of nitrogen, resists the deoxidizing action of copper. Nitrous acid, which yields a third of its oxygen to copper, undergoes no change in the presence of phosphorous and hydrochloric acids, although both convert the hyponitric into nitrous acid. With respect to nitric acid, it would without doubt be a far more powerful oxidizing agent than the hyponitric acid if it could exist *per se*.

On the part which Hyponitric Acid acts towards Organic Substances.

22. The property of hyponitric acid, of raising most bodies to their highest degree of oxidation, is owing to its little stability. This is also one of the causes which deprives it of one of the most essential characters of acids; it has no other function than that of oxidizing, for it cannot combine with chlorine under whatever circumstances these two bodies may be placed, whether brought together, *in statu nascente*, in the presence or absence of water; at a moderate or low temperature, even in the presence of a powerful base‡, chlorine is instantly disengaged, as the ac-

* Berzelius's *Jahresbericht*, 1841, p. 31.

† The nitric acid considered in the state $NO^5 + aq$.

‡ For instance, when hydrochloric acid is passed over nitre. When this salt is perfectly dry, no effect is produced at the ordinary temperature; but if it be gently warmed, or the nitre is not perfectly dry chlorine, water and nitrous vapours are formed, products which arise from the influence of the water on these vapours, and there remains chloride of potassium.

tion (19.) always occurs between the hydrogen of the hydrochloric acid and the oxygen of the nitric acid. No other combination of this acid with a simple body than with oxygen is known; and it is probable that it will never be possible to produce one, it being so with regard to chlorine, which, from its great analogy with oxygen, in respect of polarity, is capable of acting an analogous part, like this metalloid.

The hyponitric acid does therefore not behave in the way of the compound radicals: can it be admitted that it acts the part of a simple body in some organic compounds? In the present state of science this is a question of the highest importance, and it is even probable that the future chemistry of the compound radicals greatly depends on the accurate solution of this question.

23. On acting upon an organic substance and on an oxidation of an equivalent of hydrogen, the nitric acid forms, according to the supporters of the theory of substitutions, $(M - H + NO^4)$ as soon as the analysis of the new compound has shown that M in losing H has combined with NO^4. According to Berzelius, however, the new compound would be represented by the formula $(M + O - H) + NO^3$; and we might even obtain combinations such as

$$[(M + O^2 - H) + N^2O^3], \qquad [(M + O^3 - H^2) + N^3O^3]*.$$

Consequently, according to the first hypothesis, the new compound corresponds to that on which the nitric acid acted, while, according to the second, it is composed of nitrous acid and an oxide with a compound radical.

We have therefore two hypotheses which lead to very different theoretical considerations, for they proceed from a class of compounds which are not identical. Investigations, whose object is to support one or other of these hypotheses, are in the present state of science of the more importance, as the confirmation of one of them will add considerably to our knowledge of the constitution of the organic compounds, and raise their study to the rank of an exact science.

* As we cannot enter into the details of these two hypotheses, we leave out of consideration the circumstances in which the processes appear to be different where the nitrogen and the nitric oxide enter into the compound radical. My object is only to place the fundamental principles of these two modes of viewing the subject in parallel.

24. *It is evident from the preceding experiments and considerations, and, above all, from the action exercised by hydrochloric acid upon the nitrate of potash, that the hyponitric acid does not act the part of a radical in organic bodies.*

Before I had established this fact, I believed in the hypothesis of MM. Dumas and Couërbe. The results to which I was led in other investigations respecting the nature of the oxy-sulpho-sulphuric acid, were not without influence on my view concerning that of the hyponitric acid; on the other hand, not being acquainted with any very definite properties of this acid, and regarding it as a dehydrogenizing body similar to chlorine, I was naturally led to consider it as a radical like this latter metalloid, which is capable in several cases of replacing the hydrogen in organic compounds. It is precisely this dehydrogenizing property of the hyponitric acid owing to which the elements of this acid are met with in some of the compounds formed under its influence, just as we meet with chlorine in a body which has yielded hydrogen to this metalloid by substitution.

However, although hyponitric acid is capable, in the presence of some organic bodies, of functioning in an analogous manner to chlorine, yet it has never been proved that it acts like this metalloid under circumstances where it should behave like a simple body. Since, therefore, the hypothesis of the function of this acid merely rested upon theoretical observations and not upon a single well-established fact, it was requisite to support it by accurate facts. But since the investigations we have instituted have demonstrated that the hyponitric acid cannot even act the part of a radical towards that body, which in respect to polarity has the greatest analogy to oxygen, we have endeavoured to explain the action of this acid upon organic bodies in another manner, considering it as oxidizing and dehydrogenizing at the same time. In this way we were led to examine the theory of Berzelius, free from any preconceived opinion, and we have found it to correspond so well with the state of science, to explain so satisfactorily most of the facts which have been observed, that we do not hesitate to adopt it, excepting only some restrictions.

25. *That hyponitric acid acts towards organic bodies the part of an oxidizing and dehydrogenizing agent is a natural consequence of its oxidizing power*; for an organic body yields on its metamorphosis a compound which is the more stable the more com-

plete the change. Hyponitric acid, when it partially dehydrogenizes a body, or forms a compound upon which it no longer exerts under the altered circumstances any further dehydrogenizing effect, is able to convert this body into an oxide, an acid, and sometimes even into a salt.

26. The oxide may combine at the moment of its formation with the nitrous acid, whose oxidizing power is smaller than that of the other two acids of nitrogen*.

When the oxide formed does not enter into combination, it is still subject to the influence of the oxidizing agent, becomes more highly oxidized, and converted either into a simple non-nitrogenous acid (action of nitric and hyponitric acids on the essential oils which contain no oxygen, on paraffine, &c.), or into a nitrogenous conjugated acid (nitronaphthalinic acid, &c.).

Lastly, if the acid acts upon an oxy-salt which has originated under its influence, a still higher oxygenized salt may be formed (action of nitric acid on naphthaline, benzine, &c.). Even with other acids than those formed under the influence of these acids, oxidation might result (action of hyponitric acid on neutral fatty bodies).

The formation of the organic non-nitrogenous acids under these circumstances, and the action of hyponitric acid upon the fats, are facts of the highest importance in proof that this acid does indeed act the part of an oxidizing and dehydrogenizing agent.

But if an oxy-acid with compound radical containing hydrogen can be formed by the oxidizing action of hyponitric acid, it may as easily happen that by the action of this very same acid, or of nitric acid upon another organic body, bases might be formed, for acidity and basicity depend on the opposite tendency resulting from the grouping of the molecules, on the circumstances under which this grouping took place, on the proportions in which the bodies combine, &c. There is nothing therefore to prevent a base being formed, and by combining with the least powerful of the oxidizing agents resulting from the partial deoxidation of the nitric and hyponitric acids, yielding a nitrous salt (26.).

27. If, for instance, concentrated nitric acid be allowed to act upon acetone, $C^6 H^6 O^2$, two compounds are obtained, ($C^6 H^3 O + NO^3$), ($C^6 H^3 O + HO$), resulting from the dehydrogenizing

* From the examples which will be subsequently related, it will be seen that this actually happens.

effect of this acid; the elements of the base $C^6 H^3 O$ are here present in the acetone.

But if this acid be made to act upon mesitylene, it has likewise an oxidizing effect; we obtain

$$C^6 H^4 + NO^5 = (C^6 H^4 O + HO) + NO^3,$$

because the radical $C^6 H^4$ requires oxygen to form a base. The proof that the reaction takes place in the manner indicated by the above equation, is that chlorine forms with the same substance a compound corresponding to the base of the nitrite of the oxide of pteleyle by its dehydrogenizing and chlorizing action.

Owing to the existence of the radical pteleyle, which forms with oxygen an oxide that sometimes combines with nitrous acid, sometimes with water, chlorine and nitric acid furnish compounds with mesitylene which cannot be compared, although in principle the reaction of these agents is identical; be it however well understood according to the hypothesis of Berzelius, for it is impossible to account for it according to that which regards hyponitric acid as a radical, since nitric acid in its reaction on mesitylene yields no compound in which hyponitric acid makes its appearance as a constituent, and consequently no compound having an analogous composition to the product of the reaction of chlorine upon mesitylene.

28. On adding water to a hot solution of benzine in red nitric acid, there is formed

$$C^{12} H^5 + NO^4 = (C^{12} H^5 O + NO^3);$$

and the proof that this new compound does not correspond to the compound $(C^{12} H^5 + SO^2)$, but is a salt formed by the union of the protoxide of benzine with the nitrous acid, is, that when the solution of this salt in red nitric acid is raised to boiling, the protoxide of benzine is converted into oxide of benzine, and the salt $(C^{12} H^5 O^2 + 2NO^3)$ is formed.

29. Toluine also forms a nitrite of the oxide of toluine by the action of boiling red nitric acid; on the contrary, a nitrite of the protoxide is formed at the ordinary temperature (Deville).

30. On treating naphthaline with boiling nitric acid until the oil which forms on the surface of the liquid has lost the property of naphthaline, there is obtained, according to M. Laurent, a compound $(C^{20} H^7 + NO^4)$. M. Berzelius urges against this view, that if this body were so composed, the nitrite of the oxide of ethyle must be considered as $(C^4 H^5 + NO^4)$. I may add, that paranaphthaline yields under the same circumstances a

non-nitrogenous compound, and that nitronaphthalase, by a somewhat prolonged action of nitric acid, is converted into nitrite of the oxide of naphthyle,

$$2(C^{10} H^{3\frac{1}{2}} + NO^4) = (C^{20} H^7 O^2 + 2NO^3)^*,$$

just as the nitrite of the protoxide of benzine and toluine are converted under the same circumstances into peroxide of benzine and toluine.

Nitronaphthalese ($C^{20} H^7 O + NO^3$) and nitronaphthalase ($C^{20} H^7 O^2 + 2NO^3$) are therefore haloid combinations, which may be designated by the names of protonitrite of naphthyle and pernitrite of naphthyle, *naphthyle* representing the radical $C^{20} H^7$ of naphthaline.

31. The preceding examples have shown that, with the assistance of heat and of nitric or hyponitric acid, an oxide of a radical may be converted into one of higher degree; but since this radical is formed under the dehydrogenizing action of these acids, and the oxides are generated by the oxidizing effect of the same agents, it will be easily conceived that if the action is allowed to continue longer, or is rendered more powerful, the radical may be at the same time modified, and oxides produced containing more oxygen than those previously formed.

In fact, M. Laurent has observed that when the acid solution of the nitrite of the oxide of naphthyle is kept boiling until an oily body separates, a compound is formed to which the French chemist has applied the name of nitronaphthaleise, but to which the name of nitrite of the oxide of naphthaleine (*azotite naphthaleisique*) is more applicable in reference to the formula ($C^{40} H^{12} O^5 + 5NO^3$), which probably expresses its composition.

When naphthaline is boiled four or five days with nitric acid, the preceding compound is converted into nitronaphthalise, or into the compound ($C^{20} H^5 O^3 + 3NO^3$), which, like those above mentioned, contains as many equivalents of acid as there are equivalents of oxygen in the base. The new salt is consequently the nitrite of the oxide of naphthalise.

32. The compounds just considered, instead of being composed of an oxy-base and nitric acid, rather contain as the electro-negative constituent, the least powerful oxidizing agent of the three

* The analysis of this compound gave 2·90 hydrogen. According to calculation only 2·41 should have been obtained, supposing the compound to contain only 3 at. of hydrogen to 10 at. of carbon. But since 2·41 : 2·90 : : 6 : 7·22, it follows that the empirical formula is not $C^{10} H^3 NO^4$, but $2C^{10} H^{3\frac{1}{2}} NO^4 = C^{20} H^7 N^2 O^8$.

oxy-acids of nitrogen, because nitric acid, as a powerful oxidizer, is not able to expel the nitrous acid from its compound without altering the radical of the base*. But when this change has taken place, the nitric acid then acts with far greater energy; the new radical is always more stable than the former one (25.), and it is able to form a more stable base with the oxygen, and in this way the generated oxide can combine with a more powerful acid, even though this is one of the most powerful oxidizing agents.

In this way are formed by a great metamorphosis two acids, by means of nitric acid, from *indigo*, in which the presence of nitric acid is rendered probable; and resulting from a similar change which naphthaline undergoes by the action of the same acid, there is produced a conjugated acid ($C^{16} H^3 O^5 + NO^5$) + 2HO.

It is for the same reason that in the direct action of nitric acid upon pyroxylic spirit, the oxide of methyle combines unaltered with this acid, while the less stable base of alcohol reduces the nitric acid to a less powerful oxidizer, nitrous acid (21.), which is capable of combining with another unaltered portion of the oxide of ethyle.

33. So far no difficulty occurs in the explanation of the phænomena to which the nitric and hyponitric acids give rise in general in their reaction upon organic bodies. The reason is that we have admitted the hypothesis of M. Berzelius as correct, according to which the organic combinations containing oxygen consist of these metalloids combined with radicals. But this hypothesis, far from being opposed to the facts with which organic chemistry has become enriched within the few last years, is rather confirmed by the constitution and properties of the products from the reaction of several oxidizing agents upon a large number of carburetted hydrogens; by the constitution of the æthereal compounds and their analoga; by the various oxides of acetyle, formyle, &c.; by the circumstances attending the formation of the artificial valerianic acid; by the analogy of constitution of margarylic and hypomargarylic acid; by that of proteine and

* Like the compound æthers, the salts of this class cannot be subjected to Berthollet's law, as the nitric acid, in order to expel the nitrous acid from its combination, must act with an energy which is accompanied by the partial or entire decomposition of the radical. The discovery of the cause of this anomaly would be without doubt one of the greatest that could be made in organic chemistry.

of the two higher oxides than that of this regenerating substance; by that of œnanthic and azoleic acids; by that of oil of bitter almonds and of the sulpho-picroamyle; by the composition, properties and circumstances attending the formation of xanthic oxide and uric acid; by the analogy of constitution of several chlorides of compound radicals without any amount of oxygen, and of oxides of the same radicals; by those of indenigene and the oxide of indene; by the oxides of isatene; by the action of hydrosulphuric acid upon the nitrites of the protoxides of naphthaline and benzine, whence

$$(C^{20}H^7O + NO^3) + 6HS = (C^{20}H^7 + Ad) + 4HO + 6S,$$

$$(C^{12}H^5O + NO^3) + 6HS = (C^{12}H^5 + Ad) + 4HO + 6S,$$

amidides of the radicals of the bases of these salts result. Lastly, it is well known to every chemist that the constitution of the compounds derived from cacodyle were foreseen and pointed out by the celebrated Swedish chemist, at a time when these compounds were thought to possess a totally different constitution to that at present assigned to them, and that Bunsen was thus induced to endeavour to isolate the radical.

34. However, this hypothesis, although it has a number of facts in its favour, cannot be generally correct, as it starts from the law admitted in organic chemistry, *that each oxidized compound of the first order is the oxide of a radical*, a law which does not hold good for the compounds WoO^2Cl, Ur^2O^2Cl, CrO^2Cl, $(KO\,CrO^3 + CrO^2Cl)$, SO^2Cl, $(SO^2Cl + SO^3)$, and in many other combinations. And for this reason, Berzelius, in order not to come in opposition with his hypothesis, has considered these bodies notwithstanding most beautiful analogies as compounds of the second and third order. The combination of Prof. Henry Rose, for instance, is composed, according to the Swedish chemist, of sulphuric acid and chloro-sulphuric acid,

$$3(SO^2Cl + SO^3) = SCl^3 + 5SO^3.$$

And Peligot's salt of

$$(KO\,CrO^3 + CrO^2Cl) = (KCl + 2CrO^3).$$

With respect to the acid of M. Pelouze, it might be regarded as possessing an analogous composition to the sulphate of nitric oxide; but since I have proved that sulphuric acid enters into no combination with nitric oxide and sulphurous acid acts the part of a radical towards sulphur, we are compelled to look upon these combinations as having, like oxy-nitro-sulphuric acid, an analogous composition to the oxy-sulpho-sulphuric acid.

35. Benzamide, oxamide, salicylamide, phtalamide, and several analogous oxidized compounds, are composed, just like the oxidized combinations of the above class, of two radicals. The oxygen is therefore able to contribute to the formation of compound radicals, and these, by combining with oxygen, chlorine, sulphur, &c., may form oxy-acids, oxy-chloro-acids, oxy-sulpho-acids, oxy-bases, oxy-chloro-bases, oxy-sulpho-bases, and also compounds in which the oxygen, chlorine, or the sulphur acts both as acidifier as well as restorer of bases.

But since chlorine or sulphur may behave as electro-negative element towards an oxygeniferous radical, and oxygen is likewise capable of acting the same part towards the same radical, it results that the entire amount of oxygen of an organic compound is not always consumed in the formation of bases and acids, in which neither chlorine, nor sulphur, nor any other body functioning as electro-negative element towards the radical, enters.

The hypothesis of Berzelius, as well as the principle from which it is deduced, may consequently be sometimes deficient. A remarkable relation between two branches of science devoted to the study of bodies, which, without being of the same nature, are nevertheless formed and changed according to the same laws, the same principles, and frequently even according to the same theories! This it is indeed which gives a character of probability to the hypothesis of the Swedish chemist, which the opposite hypothesis does not possess, which assumes that the hyponitric acid may replace the hydrogen in a compound radical without its being capable of proving that this acid acts the part of a simple body.

On the Constitution of Hyponitric Acid.

36. The property of nitrous acid of combining with sulphuric acid, compared with that of the same acid of forming with nitric acid hyponitric acid, and the decomposition of the latter acids by bases, induced Berzelius at first to admit that this compound consisted of nitrous and nitric acid.

37. But when M. A. Rose announced that he had obtained the sulphate of nitric oxide, the Swedish chemist, in accordance with the German, considered the hyponitric acid to have an analogous constitution.

As both these views do not correspond well with the law of

multiple proportions, it remains to be seen whether the hyponitric acid is a distinct oxide of nitrogen or not.

38. If, for reasons on which the first hypothesis is founded, the hyponitric acid were composed according to the formula $NO^3 + NO^5$, nitrous acid should consist of $2NO^2 + NO^5$, on account of the action which an excess of nitric oxide has on the nitric acid, and the property which the body generated by this action possesses of being decomposed into the binary compounds which had formed it, when brought into the presence of water or any base. However, nitrous acid yields no chlorine with hydrochloric acid; it contains therefore no nitric acid, and we may thence conclude that the hyponitric acid likewise contains none.

39. If the hyponitric acid were constituted according to the formula $NO^2 + 2NO^5$, nitric oxide should be disengaged in the reaction of hydrochloric acid upon a solution of this acid in concentrated sulphuric acid, which however is not the case.

40. This question may be otherwise solved if we take into consideration the amount of stability, and then two things are to be considered. The first is the relative stability of the compounds NO^5 and NO^4, and the second that of the acids $HO + NO^5$ and $NO^3 + NO^5$, or $NO^2 + 2NO^5$.

The greater stability of NO^4 in comparison to NO^5, may be ascribed to a similar cause as that which produces the relative stability of the compounds NO, NO^2, NO^3, NO^4. It may likewise be ascribed to the affinity of NO^5 for NO^3 or NO^2. In the first case, the hyponitric acid is a distinct oxide of nitrogen, in the second it is not.

If this acid is composed according to the formula $NO^3 + NO^5$ or of $NO^2 + 2NO^5$, it must be more permanent than $HO + NO^5$, because the former can be produced by the action of nitric oxide upon the second, and because the stability of a compound depends on its affinity, or is otherwise proportional to the affinity of the binary compounds which constitute these combinations*. Now the preceding observations and considerations show that the hyponitric acid is less stable than the hydrated nitric acid, consequently that it is not a combination of nitric acid with nitrous acid or nitric oxide.

* Supposing the bodies to be under the same conditions of existence as in the above case.

Article XV.

On the Incandescence and Fusion of Metallic Wires by Electricity. *By* Peter Riess*.

[Extract from a paper read before the Academy of Sciences of Berlin, June 5, 1845.]

THE extraordinary effects of electricity related by the ancients, as the type of which may be mentioned the melting of a sword in its uninjured scabbard, have led to a remarkable hypothesis concerning the melting by lightning or by electricity in general. Franklin, in the year 1747 †, assumed that electricity dissolved the cohesion of a metal without the aid of heat, and thus effected a cold fusion. When however it was discovered that a bell-wire melted by lightning singed the wood-work of a room, and Kinnersley found that electricity artificially excited heated a piece of metal so much the more the smaller it was in section, that therefore lightning might produce heat sufficient to melt the point of a rapier without materially warming the other part of the blade, Franklin retracted his assumption ‡, and severely reproved himself for having grounded it upon a fact not sufficiently established. That great man evidently was not just towards the opinion which he had formed fifteen years previously; if the story of Seneca gave rise to the assumption and retention of his hypothesis, it certainly was not its chief support, but it was founded on the idea that igneous fusion differed from that effected by electricity. It is not therefore surprising that the idea of a cold fusion was again taken up forty years later by Berthollet §, who explained every action of electricity upon a substance as a forcible separation of its particles, and considered the heat which occurs on its melting, and which he, led into error by inaccurate experiments, rated at far too small a quantity, as a secondary phænomenon.

The hypothesis of fusion brought about by a primary action of electricity has experienced the sad fate of being partly for-

* Translated by Edmund Ronalds, Ph. D.
† Experiments and Observations. London, 1774, p. 52.
‡ Ibid, p. 419.
§ *Chemische Statik*. Berlin, 1811, vol. i. p. 270.

gotten and partly used, like the anecdote of Charles the Second's fish, as a warning against all hypothesis. Since Van Marum with every assistance made a series of valuable experiments upon the effects of an increased power of electricity, we have contented ourselves with enumerating these experiments one after the other. Indeed, we have gone a step beyond Van Marum. When the Dutch philosopher expresses his astonishment at some of the effects of electricity, he means to hint, that he has sought for some connexion between them, and that some band of union should be sought for. In the manuals of natural philosophy, however, it is stated, without further remark, that electricity causes heating effects, amongst which are reckoned the incandescence, melting, and reducing to dust of the metals; that it also exerts mechanical action, on which occasion the rending of imperfect conductors is mentioned; and, lastly, that it occasions chemical decompositions. Such a division of the phænomena is not at all suited to convey a right impression of the mode of action of the electrical discharge, and has indeed prevented us for a long time from forming a correct idea of what really does take place. For, so long as incandescence and fusion by means of electricity were considered as the direct result of the heat excited, it appeared sufficient to examine the laws of the electrical excitation of heat between any two points on the scale of temperature, which, as it was necessary to use the air thermometer, could not be chosen for a range of temperature widely differing from that of the air.

I have submitted to fresh examination the effect of electrical discharges gradually increasing in power upon wires, and have found that, for a discharge of a certain power, the appearances of heat and mechanical action are simultaneous, and that therefore Franklin's hypothesis of cold fusion is not further from the truth than the one commonly adopted of hot fusion. At the same time I discovered a difference in the manner in which electricity was propagated in good conductors; it appeared to me worthy of notice, as it explains many electrical actions which have hitherto been isolated facts. In the following extract those experiments are described, the wires of which have been preserved fixed upon paper with amber varnish. It appeared to me that a drawing of these specimens could not be executed with sufficient accuracy to increase the clearness of the description.

The Melting-point calculated from observed increase of Temperature.

A thin platina wire inclosed in the ball of an air thermometer was taken of different length in four successive series of experiments, and the heat excited in it, by different discharges, varying in power, of an electrical battery, was observed. This heat might have been calculated by the formula which I formerly established *, when the two constant quantities of the formula had been determined. The following sufficiently close accordance between the observation and calculation occurred.

	Temperature for unity of charge.	
Length of wire.	Observed.	Calculated.
141·6 lines	0·270 C.	0·2688
91·66 ...	0·338	0·3419
48·75 ...	0·449	0·4461
34·75 ...	0·495	0·4953

The shortest wire was still too long to be melted by the battery used; I shortened the wire therefore to 15 lines, and was then enabled to fuse it with the quantity 38 of electricity contained in four jars, or with the quantity 42 contained in five jars. If the formula be applied to these cases, we obtain as the temperature of the consumed wires 211·8 and 207·0 degrees of the centigrade thermometer, temperatures insufficient to raise to red heat, much less to fuse platina.

These temperatures could also be calculated from other observations. There was constantly in all these experiments a thick platina wire forming part of the connecting circuit of the battery, the increased temperature of which was observed, that bearing, according to the formula mentioned, a definite relation to the rise of temperature in the thin wire. This calculation likewise corresponded sufficiently with the observation.

	Increase of temperature in the thin wire.	
Length of wire.	Calculated from the increase of temperature in the thick wire.	Observed.
141·6	0·2792	0·270
91·66	0·3346	0·338
48·75	0·4427	0·449
34·75	0·4906	0·495
15·0	0·6792	

* Poggendorff's *Annalen*, vol. xlv. p. 23.

The temperature of the thin wire 15 lines in length would therefore be 0·6792 for unity of charge, and for the destruction of the wire 239·6 and 245·2 degrees. It is remarkable that these temperatures are in no way less than those found previously. For when, as is really the case, the observations on the thick wire give a higher temperature for the thin wire than the observations on the thin wire itself, the supposition is thereby contradicted, that the retarding power of the thin wire does not decrease in a constant ratio with its diminution in length, but only within a certain limit, which is above the length of 15 lines. It must also be noticed, that the temperatures at which this wire was destroyed are rather too high than too low, as the calculation has been made for the discharge of the whole quantity of electricity contained in the battery, although, as will be shown hereafter, no inconsiderable portion of that quantity remains behind in the battery after the discharge.

It requires no very extended process of reasoning to show that the temperature of 245 degrees (the highest calculated from any single experiment) is not that really possessed by platina fused by means of electricity. By a smaller quantity of electricity than that here used, platina is fused into small shining globules, which are often so firmly melted into the sides of a glass tube held at a quarter of an inch distance, as only to be removed by fracture of the glass. The detailed experiments prove that the electrical fusion of metals is no secondary phænomenon to their being heated, and that a metal actually melts long before the rise in its temperature would cause it to do so. We must therefore acknowledge in the fusion an electrical action distinctly separate from that causing heat by electricity, the laws regulating which action must be studied apart. This separation of the two phænomena, which has thus been indirectly found, may be seen in a clear and direct manner, if the attention be directed to the state of the wire exposed to the electrical discharge during its transition from a normal rise in temperature to the melting-point. Before that power of discharge has been attained which would cause the wire to become red-hot, peculiar changes in the appearance of the wire occur; and in the same way before it reaches the melting-point it is affected in a manner, having no resemblance to that produced by a mere rise of temperature.

Appearances which precede and accompany the Heating to Redness.

Vibration—Vaporization.

The battery which I used consisted of five jars, each of which contained a covered surface of one and a half cubic feet; it would not however bear the charge which was necessary for many of the following experiments: I therefore changed it for one consisting of seven jars, each containing 2·6 cubic feet of coated surface. These jars stand upon a wooden frame 27 in. in diameter, insulated by glass feet, and covered with tin foil; they are supplied with *f*-shaped pieces of metal in contact with their interior surfaces, and moveable on hinges, by means of which any number of them can be brought into connexion with each other. The unit jar, by means of which the charge of the battery was measured, had, as before, half a cubic inch of covered surface; its balls were also at half a line distance from each other, but I now took as unity the quantity of electricity causing two explosions. This unity is in future also understood for those experiments which were made with the old battery, in which case the number of jars will be denoted by an asterisk.

A platina wire, 34 lines in length and 0·0209 line radius, was inserted by means of two strong springs of bell-metal in the connecting circuit of the battery. On the discharge of increasing quantities of electricity the following appearances were observed in the wire.

Experiment 1.

Number of jars.	Quantity of electricity.	
4*	5	The wire vibrates violently.
	7	A streak of vapour rises from it.
	9	No vapour—slight bend in the wire.
	11	The bend increased and a new one formed.
	13	The wire is red-hot and bent in many places.
	15	The wire is white-hot, with so many bends as to be tightly stretched.

Experiment 2.—Another platina wire, 16 lines in length and with a radius of 0·0261, gave the following signs:—

Number of jars.	Quantity of electricity.	
4	6	A spark on the inner side of the wire, on that side nearest to the inner surface of the battery.
	8	Streak of vapour the whole length of the wire.
	9	Vapour—spark on the outer side.
	10	The same.
	11	No spark or vapour—deep bend.
	12	Spark on the outer side—increased bend.
	13	The wire is red-hot.

Experiment 3.—On a considerably thicker wire (radius 0·04053) the following effects were observed:—

Number of jars.	Quantity of electricity.	
4	12	
	14	Spark on the outer side.
	16	Spreading spark on the outer side.
	18	Bend in the wire.
	20	The same increased.
	22	Several bends.
	24	The same increased.
5	26	The same.
	27	The wire is red-hot.
	28	The wire glows brightly—many deep bends.

Long before the amount of electricity has been attained necessary to produce a red heat, the effects observed on the wire prove that the electricity has penetrated it in a powerful manner. The wire is visibly shaken, small sparks appear at its ends, and particles are forcibly torn from its surface, which rise from it in the form of a dense vapour. It often happens that contemporary with the spark larger pieces of metal are thrown off, which being red-hot give a spreading appearance to the spark. These effects are never entirely wanting, but they are not constant in intensity. The vibrations are so much the more obvious as the wire is easily put in motion, and the size of the sparks at the ends depends upon the material of the wire, and upon the form and material of support. In the present instance, when the wire lay in rounded clamps of bell-metal, the sparks were powerful

from wires of platina, palladium, and German silver; less brilliant with silver and brass: they were not at all seen with copper. The spreading of the sparks depends upon the brittleness of the metal and its affinity for oxygen; it did not appear with silver, and with the other metals only in short flashes; but with iron very extensively. The formation of the cloud of vapour is much more constant than the appearance of the sparks, and did not fail in any metal. The facility with which the vapour is formed varies with the different metals, but not in a greater degree than with different wires of the same metal. A certain sort of platina wire produced vapour so copiously, that on the first discharge, each time, a streak of vapour was formed over the whole length of the wire, with other kinds only partial streaks appeared. Sometimes the formation of vapour only occurs at one discharge and not at the succeeding ones: sometimes, however, it is seen in consecutive increasing discharges, but then with decreasing force. The formation of vapour is essentially promoted by a peculiar state of surface in the wire, and the greater or lesser number of furrows left by the wire drawer on the wire appears to have considerable influence upon it. I have sometimes remarked, that by carefully polishing a wire the production of vapour took place in a less degree than was otherwise the case with the same kind of wire.

Bending of the Wire.

The phænomena observed on the wire are worthy of notice, as they show the powerful effect exerted upon it long before it is brought to a red heat by the electrical discharge; but the stage or period of their appearance and their intensity depend, as has been remarked, much upon casualties. A better drawn, more firmly connected wire, will only show the spark, the vapour, and perhaps even the violent vibration with the application of a greater quantity of electricity, than a wire less carefully prepared. We cannot therefore conclude in general, from the appearance of such phænomena, that a certain increase of power of discharge will bring a wire to a red heat. It is however different with the permanent change in the wire, which must now be noticed, and which is intimately connected with the incandescence, and occurs immediately before it,—I allude to the angular bend in the wire which suddenly takes place at the discharge, as if a sharp-edged instrument had been pressed upon it. On the first dis-

charge, this bend merely appears as a break in the brilliant line of light which is reflected from a polished wire by daylight; on the repetition of the same discharge, or by increasing it, the bend is deepened until it becomes a measurable angle. A platina wire (radius 0·021) was exposed to the following discharges:—

Experiment 4.—

Number of jars.	Quantity of electricity.	
3	8	Sparks on the outer side of the wire—vapour.
	9	Violent shaking—bend.
	10	Bend deepened.
	10	The same—fresh bends.

This wire presents, at a considerable distance from its fixed points, a deeply impressed angle, and on the right-hand side of that several slight bends. Four other platina and two iron wires, which were likewise exposed to a few discharges, received in the same manner deep bends. Wherever the bending takes place without obstruction, it is obtuse-angled: in several cases I measured it, and found it to vary little from 110°. Neither the dimensions nor the material of the wire cause this to vary, as was shown by a thick platina wire (radius 0·0405), an iron wire and a copper wire. The formation of the angle is rendered difficult, and partly obstructed, if the wire be stretched in a straight line or exposed to considerable tension in an arched curve. Then, instead of the deep bends, only slight indentations appear in great number, which easily escape observation: sometimes the wire breaks at that part where the angle would have been formed, and the wire is hindered from yielding. For the same reason, an angle already formed hinders the production of a new one, and in this manner it is that the different distortions of the wire are caused, of which I shall speak directly. The bends occur on the discharge of a less quantity of electricity than is requisite to produce a red heat. The degree of incandescence distinctly visible by daylight has been taken in these experiments as the normal quantity, but I have satisfied myself, that in complete darkness the formation of the first bend is attended with no appearance of light (with the exception of occasional sparks at the connecting points of the wire). If more powerful discharges are allowed to pass through the wire after the first bend, new bends will constantly appear, which, modified by those already present, or distorting them, cause curves and angles in different planes, and

give a ribbed, wave-like appearance to the wire. This wave-like appearance is also produced by repeated discharges of that quantity of electricity which causes the wire to become incandescent.

All the wires hung whilst red-hot in a wide arc; had they been suspended from one end and a weight attached to the other, instead of bends, merely slight indentations would have been observable in them. Hence the remarkable circumstance is explained, why, notwithstanding the number of observations on the fusion by electricity, the phænomena of bending has only been discovered in very recent times. I believe myself to have been the first who (in the year 1837) called attention to the angular bends in a wire subjected to the electrical discharge*. Two years later†, the younger Becquerel makes mention of the wavé-like bends in very thin platina wires (he could only produce them in wires of 0·016 line radius) which had been exposed several times to a red heat; he however misconceives their importance, considering them as the effect of the incandescence, and as having no connexion with the shortening of the wires, to which we shall now proceed.

Apparent shortening of the Wires.

Nairne made the discovery in the year 1780‡ that wires made red-hot by electrical discharges were shortened. An iron wire of 0·06 line radius and 10 inches in length, measured only 8·9 inches after fifteen energetic discharges from a powerful battery had been passed through it; it had therefore been shortened one inch. The wire retained its original weight, but measured with the callipers it appeared to have become thicker. Van Marum shortened a wire 18 inches in length and 0·109 line radius a quarter of an inch by a single discharge, and assumed, without proof§, that the discharge of the electrical current had flattened the wire sideways, and that consequently it had become shorter.

From these few superficial experiments, it was declared universally, without hesitation, that metallic wires were expanded in thickness, and consequently shortened, by the passage of electricity through them‖. Even quite recently, the younger

* Poggendorff's *Annalen*, vol. xl. p. 340.

† *Ann. de Chimie*, 2 ser. t. lxxi. p. 44. Poggendorff's *Ann.* vol. xlviii. p. 549.

‡ Philosophical Transactions for 1780, p. 334.

§ *Beschreibung einer grossen Elektrisirmaschine*, erste Fortsetzung. Leipzig, 1788, p. 13.

‖ Gehler's *Neues Wörterbuch*, vol. viii. p. 541. Biot, *Lehrbuch von Fechner*, vol. ii. p. 266.

Becquerel, to whom the bends in the wires were known, has endeavoured to establish a law for the shortening of platina wires in proportion to their diameters, assuming without further proof that the shortened wires had become thicker*. I have found it necessary to institute new experiments upon this subject.

Experiment 5.—A platina wire, 0'''·02089 radius, the length of which, 42·66 lines, had been accurately determined, was fixed horizontally in the spring clamps of the connecting circuit. The quantity of electricity 5, collected in 4* jars, was discharged eleven times, and the quantity of electricity 7 was discharged six times through the wire. The discharges of the smaller quantity of electricity had no visible effect upon the wire; those of the larger quantity produced two deep bends. When the wire was drawn tight its length was exactly 42·63 lines, therefore the same as before the experiment.

Experiment 6.—A platina wire of the same thickness was loosely laid in the clamps, and after each discharge drawn tolerably tight and measured.

Number of jars.	Quantity of electricity.	Appearance of the wire.	Length of the wire in lines.
			38·16
4*	10	Bends.	38·11
	...	Sparks at the ends—bend.	37·86
	...	The same.	37·76
	12	The wire slightly red-hot.	37·51
	...	The same.	37·41
	14	Bright red heat	37·21
	...	The same.	36·86

Here the wire was shortened 1·3 line; its jagged appearance, however, which could not be removed by drawing it tight, showed that the shortening was only apparent. After the wire had been drawn through the fingers, its length was 37·21, and after another smoothing 37·41. Even now the uneven surface of the wire could be seen and felt, and could only have been removed by pressure against a hard body.

Experiment 7.—A platina wire of 0·0286 radius was heated to redness ten times by discharges; its length before the experiment was 77·5 lines, afterwards 72·3. The apparent shortening of 5·2 lines was removed by drawing it once through the fingers,

* Poggendorff's *Annalen*, vol. xlviii. p. 549.

after which it measured 75·9 lines. There is no doubt that the remaining loss of 1·6 line was occasioned by very fine bends.

Experiment 8.—Lastly, I repeated the experiment upon an iron wire of 0'''·0266 radius and 98·2 lines in length, and performed the experiment in the same manner as it had been done by others. The wire was loaded with a small pear-shaped weight (12¼ grammes), it was hung vertically, the point of the weight however was supported by a piece of metal with a hole in it. After the wire had been brought eight times to a moderate red heat by discharges it measured 90·7 lines, an apparent shortening had therefore taken place of 7½ lines. By continued careful smoothing it was obtained of the lengths 95·2 and 96·5 lines, so that there remained only 1·7 line as its decrease in length; a further straightening of the wire would doubtless have restored it to its former length, but could not have been effected without the aid of fire.

The wires which served for the experiments 7 and 8 have been preserved: they appear under the magnifying-glass to be covered with a great number of minute bends, which easily account for the apparent decrease in length of two lines.

It follows from these experiments, that the shortening of wires and increase of their diameters, which have been accounted the effect of powerful electrical discharges upon them, does not take place in reality, and that the apparent shortening arises from bends which under certain circumstances are sufficiently small to escape a superficial observation. These less perceptible bends appear, with greater ones, in tightly-stretched wires when exposed to discharges which heat the wires to redness. In wires slackly suspended bends are effected, as was shown at page 439 by electrical discharges, which even in complete darkness do not produce a red heat; and these discharges would have sufficed to shorten the wires apparently, if the greater number of the bends had not been so marked as to render it impossible, on measuring, to overlook them.

Amongst the effects of incandescence produced by electrical means, a lengthening of wires tightly stretched by weights has been noticed. Kinnersley first accomplished this by loading a harpsichord string twenty-four inches in length with a pound weight and making it red-hot by an electrical discharge, after which it was lengthened one inch*. Beccaria performed the

* Franklin, Experiments and Observations, 3rd ed. p. 399.

experiment in a more complicated manner*. A metallic rod was so placed upon a horizontal plane as to be moveable round one of its ends, whilst the other finely-toothed end worked upon a cog-wheel furnished with a hand. A strong spring pressed against the rod, but was checked in its action by a stretched iron wire eight inches in length, fixed upon the rod. When the iron wire was brought to a red heat by an electrical discharge, the hand indicated a movement of the rod in the direction of the acting spring, and therefore showed a lengthening of the iron wire, and it appeared that the permanent increase in length was less than at the moment incandescence appeared. It is evident that this was not a primary electrical action, but a mechanical effect upon the red-hot wire. I therefore instituted only one experiment of this kind, in which however the wire immediately broke, in consequence of my having used either too great a weight or a too powerful electrical charge.

Laws of Electrical Incandescence.

Former Statements.

We possess no practical observations on the laws which regulate the incandescence of wires by electrical discharges. Several philosophers have indeed occupied themselves with the heating effects of electricity; but they directed their attention to the fusion of the metals, and upon that point their statements are contradictory, nor have they been able to obtain any clear insight into the nature of the phænomena. The temperature of fusion is by no means adapted for a fixed standard point, as there are different degrees of fusion, and, as will be seen below, an electrical action precedes it, which also occasions the destruction of the wires. The great diversity in the statements of those philosophers arises partly from this cause, partly however from an answer having been sought to a question which, generally put, is not capable of a definite solution.

Van Marum† charged equally a battery of 135 and one of 225 jars; he found in three experiments that the length of iron wire which could be melted by them was in the proportion of 3 to 5. Thus the length of wire melted, the intensity remaining the same, would be proportional to the quantity of electricity. The lengths of wires of different thicknesses, which were melted by a cer-

* *Elektric. Artific.* Torin, 1772, p. 301.

† *Beschreibung*, &c. Erste Fortsetzung, p. 3.

tain constant charge, bore no relation to the diameters of the wires*.

Cuthbertson disputed the accuracy of Van Marum's experiments, and asserted that with equal intensity four times the length of wire was melted by a double quantity of electricity, and three times the length by one and a half times the quantity necessary to melt a single length of wire†. Brook assumed‡ that the effect of electricity upon wires increased as the squares of the quantities of electricity used, so that two jars charged to a certain degree would melt a four times longer wire than one jar charged to the same degree. Singer§ admits the law of the squares for moderate lengths of wire only, as with longer wires a portion of the electricity collected in the battery is lost. It is also stated that a certain quantity of electricity will melt the same length of wire, whether it be accumulated in one or two jars.

A discussion of these statements, no single one of which can be valid in all cases, is for this reason impossible, because no mention has been made of the connecting circuit that was used, that is, of that part of the wire which was not melted. At the time that those experiments were made, an opinion was prevalent that the effect of the electrical battery was solely due to the quantity of electricity and to the number and condition of the jars that were employed, an opinion which, although it has been occasionally repeated in modern times, calls for no express refutation, as every well-conducted experiment with electricity in motion at once disproves it.

The laws of incandescence can be expressed in the simplest manner by the increase of temperature in a wire of constant dimensions included with the incandescent wire in the connecting circuit. In all the following experiments, therefore, I inserted an electrical thermometer in the connecting circuit, the increase in temperature of which was observed. The platina wire of the thermometer was necessarily chosen of such a thickness as to remain uninjured on the application of the most powerful discharges. In order to obtain an equally sure indication for discharges of very different intensities, the same instrument could not be used for every experiment: I made use of

* *Beschreibung*, &c. Erste Fortsetzung, p. 9.

† Gilbert's *Annalen*, vol. iii. p. 13.

‡ New Experiments in Electricity, *Encyclop. Metropolit.* Lond. 1830. Electric. p. 116.

§ *Elemente der Elektricitätslehre.* Breslau, 1819, p. 116, 117.

the two thermometers, the dimensions of which are given in Poggendorff's *Annalen*, vol. xliii. p. 49, and vol. lxiii. p. 485, and furnished them with different platina wires, the radii of which varied from 0·058 to 0·116 line, and the length from 60 to 97 lines, according as it was found necessary. In experiments which were to be compared directly with each other, the thermometer remained unchanged.

Incandescence depending on the Power of Discharge.

At some distance from the thermometer a platina wire was inserted in the connecting circuit, and the balls of the thermometer protected by screens from any external influence. A certain number of battery jars were charged with an increasing quantity of electricity, until a discharge was attained, producing visible incandescence in the wire by daylight, and each time the temperature of the thermometer was observed. This method of procedure was continued with different numbers of jars. The following series of observations show the discharges which sufficed to produce incandescence, and the attendant rise in the thermometer.

Experiment 9.—

Number of jars.	Quantity of electricity.	Increase of temperature in thermometer.
5	12	20·9
	...	20·0
3	10	
2	8	20·3
3	10	21·6
4	11	21·8
5	12	20·2
	...	20·7

Experiment 10.—A new platina wire gave the following:—

Number of jars.	Quantity of electricity.	Increase of temperature in thermometer.
2	8	20·7
7	14	20·4
2	8	20·2
	...	20·7

Experiment 11.—With a third platina wire, incandescence was observed attending the following discharges:—

Number of jars.	Quantity of electricity.	Increase of temperature in thermometer.
3	7·5	20·0
	7·5	20·0
7	11·0	20·6
3	7·5	20·4

It follows, therefore, that the incandescence of a wire, as also its increase in temperature, depends upon the square of the quantity of electricity divided by its intensity. If therefore the quantity of electricity and the number of jars necessary to produce incandescence in a wire has been ascertained, the magnitude of that product is established, and it is easy to calculate what number of jars are required for a certain quantity of electricity to produce incandescence in a similar wire. In the experiments 9 and 10, the mean of that product is = 31·0, according to which the quantities of electricity for 2, 3, 4, 5, 7 jars, would be

7·9 9·6 11·0 12·4 14·7.

In experiment 11, the product 18 gives for 3 and 7 jars the quantities 7·4 and 11·2 of electricity. These calculated quantities of electricity approach as nearly to those which were observed as could be expected from the manner of conducting the experiments. But the law thus deduced is confirmed in a far more exact manner by the observations on the thermometer, which, for experiments of this kind (when the susceptibility of the eye and the amount of light may materially modify the apparent effects), showed for all the discharges a surprising uniformity. My former experiments proved* that the increase of temperature in a wire of constant dimensions, forming part of the connecting circuit, was in proportion to the square of the quantity of electricity multiplied by its intensity, and we might therefore have deduced the law mentioned, simply from the observations on the thermometer, without having measured the quantity and intensity producing each separate discharge. But this double confirmation was not superfluous, because hitherto, where the laws regulating the rise in temperature of the connecting circuit have been applied, no part of the circuit was heated to any considerable extent.

In the sequel also the effects of the current of discharge will be compared with the amount of heat which it produces; for

* Poggendorff's *Annalen*, vol. xl. p. 342.

brevity, therefore, we shall measure the current by its heating power, and always understand by the expression, *Power of the current of discharge*, the amount of heat which it is capable of producing in a wire of constant dimensions forming part of the connecting circuit.

The contents of this paragraph may therefore be thus expressed: Whenever a wire forming part of the connecting circuit of a battery is made incandescent by the discharge, the same takes place, whatever changes may be made in the number of jars or in the quantity of electricity, provided the power of the current of discharge remain unchanged.

Incandescence of a Wire according to its Length.

In experiment 9, a platina wire of 26·6 lines in length was made incandescent by a current of discharge, the mean power of which was 20·8; in experiment 10, a wire was made incandescent by a current of 20·4; and in experiment 11, when the length of the wire was 10·7 lines, the power of the current was found to be 20·3. I took a similar wire, 49·5 lines long, and found that it became incandescent when the thermometer indicated a current of 20·8. In these experiments with wires of different lengths, therefore, very nearly the same power of current was observed.

Experiment 12.—A platina wire 15·7 lines long, became incandescent with—

Number of jars.	Quantity of electricity.	Power of discharge.
4	12	8·3
	12	8·0
7	15	7·7

Experiment 13.—A similar wire, 77·5 lines long, to be brought to an incandescent state, required—

Number of jars.	Quantity of electricity.	Power of discharge.
4	22	8·3
	22	8·0
	22	8·0

A wire therefore 15·7 lines in length was made incandescent by a current 8·0, and one 77·5 lines in length by a current of the same power, although in the latter case a much larger quantity of electricity was discharged than in the former. From this it

follows, that—*The power of the current of discharge necessary to produce incandescence in a wire is independent of the length of the wire.*

By the aid of the last two paragraphs a clearer insight is obtained into the nature of the problem mentioned before (p. 444), the experimental solution of which (if we substitute for fusion the smaller electrical effect of incandescence) has occupied several philosophers.

Let Θ be the indication of a thermometer placed in the constant part of the connecting circuit, λ, ϱ, x the length, radius and retarding power of an interposed wire, q the quantity of electricity, and s the number of jars used in the experiments. As the indication in the thermometer is proportional to the temperature of the wire extended within it, we have, if a and b represent constant quantities dependent upon the constant part of the connecting circuit,

$$\Theta = \frac{a}{1 + \frac{b\lambda x}{\varrho^2}} \cdot \frac{q^2}{s}.$$

Let this discharge suffice to produce incandescence in the included wire, the length of which is l, it is required to find the length of wire l', which would be brought to the incandescent state by the quantity of electricity nq collected in ns number of jars. The indication of the thermometer must necessarily be the same as before; we have therefore

$$\Theta = \frac{na}{1 + \frac{b\lambda' x}{\varrho^2}} \cdot \frac{q^2}{s},$$

and hence

$$\lambda' = n\lambda + (n-1)\frac{\varrho^2}{bx}.$$

Two jars charged to any amount will therefore render incandescent a wire more than double the length of that similarly affected by one jar; how much more than double the length cannot be determined for all cases; for the length λ' depends upon the nature of the wire to be heated, and upon the magnitude of the constant quantity b, which varies with the condition of the connecting circuit. The relation sought approaches so much the nearer to the relation of the number of jars used in the experiment to each other (in this case therefore as 2 to 1), as the wire to be heated is thin, and the connecting circuit is

composed of good conducting materials; if the reverse is the case, however, the relation may be much more distant. A more accurate indication of the lengths of wire rendered incandescent cannot be expected from the formula above mentioned, for, as will be shown in the sequel, the formulæ for heat are not absolutely accurate, when part of the connecting circuit is in a state of incandescence.

Incandescence of Wires according to their Thickness.

Three platina wires of increasing thickness were fixed successively at the side of the thermometer; I observed with a careful increase of charge the first appearance of incandescence in them, and at the same time the alteration in the thermometer.

Experiment 14.—

Wire.	Radius in lines.	Change of temperature in thermometer.	Mean.
1.	0·0181	8·7	
		9·0	
		9·4	
		9·0	9·0
2.	0·02089	20·0	
		20·0	
		20·6	
		20·4	20·2
3.	0·0261	42·5	
		41·8	
		44·8	43·0

The thermometer was changed for one less sensitive, and the observation continued with three other platina wires.

Experiment 15.—

Wire.	Radius in lines.	Change of temperature in thermometer.	Mean.
3.	0·0261	5·6	
		6·0	
		6·2	
		5·6	5·8
4.	0·02857	8·0	
		8·3	
		8·0	8·1
5.	0·04053	31·3	
		30·8	
		31·0	31·0

On comparing the changes in the thermometer with the radii of the incandescent wires, it is found that the former are in proportion to the squares of the squares of the latter. If we take as mean numbers 9394° for the first thermometer, and 1202° for the second, as the temperature at which a platina wire of 0·1 line radius would just be incandescent, we obtain for the alteration in the thermometer Θ, or for the power of the current of discharge, sufficient to bring a wire of r-tenths of a line in radius to incandescence, the equation

$$\Theta = \left.\begin{matrix} 9394 \\ 1202 \end{matrix}\right\} r^4.$$

From which the following series results:—

Wire	Power of current of discharge at point of incandescence. Calculated.	Observed.
1.	10·0	9·0
2.	17·9	20·2
3.	43·9	43·0
3.	5·6	5·8
4.	8·0	8·1
5.	32·4	31·0

The accordance between observation and calculation must be considered satisfactory, as to the other considerable sources of error in experiments of this kind, the difficulty is added of determining an equal degree of incandescence in wires of different thickness.

The power of current of discharge in a battery which is required to bring a wire to an incandescent state, is proportional to the fourth power of the radius of the wire.

Incandescence in Wires of different Metals.

The difficulty of determining a fixed degree of incandescence in different wires is considerably increased if the wires are composed of different metals. Not only does the colour of the metal and its greater or lesser affinity for oxygen render the observation inaccurate, but another circumstance occurs of which mention will be made at p. 455. It is not easy with some metals to keep them solid and in a state of incandescence at the same time, which is indispensably necessary to our present purpose. The wires with which the following experiments were made were applied without being submitted to further chemical examina-

tion. Only one wire, which gave an extraordinary result, and had been supposed to consist of gold, was chemically examined, and on finding it to be very impure was thrown aside. Each wire was exposed to cautiously increased discharges, and on the first appearance of incandescence by daylight the indication of the thermometer observed. When the experiment was repeated on the same wire, the indications of the thermometer are placed close together in the following table; experiments on different wires are separated by a small space. The temperatures indicated in the second vertical column were for the most part obtained several weeks later than those in the first.

	Metal composing the wire.	Radius in lines.	Indication of thermometer at the time of incandescence.		Mean.
Exp. 16.	Platina . .	0·03958	25·3	24·8	
			24·9	24·9 . .	25·0
... 17.	German silver	0·04030	25·5	25·6 . .	25·55
... 18.	Iron . . .	0·04006	19·0	19·4	
			19·8	19·4	
			19·5		19·42
... 19.	Palladium .	0·03951	26·3		
			26·4 .		
			26·8		26·5
... 20.	Brass . . .	0·02461	10·9		
			10·4		
			10·8		10·7

The following experiments were made with a more delicate thermometer.

Exp. 21.	Silver . .	0·02641	60·0		
			63·5		
			60·0	63·4	
			56·3	63·5	
			59·6		
			58·5		60·6
... 22.	Iron . . .	0·0266	11·1	11·4	
			10·8	11·4	
			11·3	11·8	
			11·6		
			11·3	11·4	
				11·0	
				11·1	
				11·2 .	11·3

	Metal composing the wire.	Radius in lines.	Indication of thermometer at the time of incandescence.		Mean.
Exp. 23.	Copper . .	0·0253	61·5	63·4	
			63·0	61·0	
			62·7	59·8	
			60·7		
			60·2	. . . .	61·5
... 24.	Platina . . .	0·0258	10·9		
			11·4		
			11·2	. . . .	11·2
		0·03879		57·0	
				56·8 .	56·9
... 25.	Brass . . .	0·02461	21·2		
			22·2		
			21·2		
			21·0	. . . .	21·4

To get rid of the influence of the different thickness of the wire, we must, according to page 450, divide each indication of the thermometer by the fourth power of the radius of its corresponding wire. We thus obtain values for the amount of heat produced in a thermometer interposed in the connecting circuit, and relative values for the power of the current of discharge necessary to produce incandescence in wires of equal thickness composed of different metals

From the mean numbers deduced from the experiments, the following series of metals, arranged according to the increased power of the current, is obtained, in which the current of discharge required by platina is taken as unity.

Incandescence appears in	with the power of the current i.
Iron	0·816
German silver	0·950
Platina	1·
Palladium	1·07
Brass	2·59
Silver	4·98
Copper	5·95

By the assistance of this table, if the incandescence of a wire be observed, with the attendant thermometrical indication, we are enabled to calculate the indication of the thermometer for

the incandescence of another wire. Thus, let the thermometrical indication, radius, and relative power of the current be,

For the first wire . . θ r i,
For the second wire . θ' r' i',

the relation existing will be

$$\theta' = \frac{i'}{i}\left(\frac{r'}{r}\right)^4 \theta.$$

If, for example, in the connecting circuit an electrical thermometer sink 25·5 degrees, whilst at another part of the circuit a German silver wire of r lines radius is made incandescent by the discharge, then if a copper wire of r' lines radius is to be made incandescent, the thermometer must sink $\frac{5{\cdot}95}{0{\cdot}95}\,25{\cdot}5\left(\frac{r'}{r}\right)^4$ degrees.

Although, from the nature of the experiments, no very great degree of accuracy can be ascribed to the numbers in the table above, still it is evident that they depend upon the power possessed by the wires of retarding electricity, and in general increase as this decreases. In addition to this, the capacity for heat and the specific weight of the wires exert some influence, which however is by no means apparent, according to the laws which I established for the excitation of heat alone*. If this indeed were the case, then the power of the current, multiplied by the retarding power and divided by the product of the capacity for heat multiplied by the specific weight, would give nearly the same quotient for every metal, which does not result.

Besides those named there are other properties of the metals which affect their incandescence, and which cannot be subjected to calculation. These are, probably, brittleness and the facility with which the metal combines with the oxygen of the air. [The more easily oxidizable metals, as iron, brass and copper, become tarnished of various colours before their incandescence.] The numbers in the series above can therefore only be valid for constant quantities, which must be determined empirically.

Phænomena which follow Incandescence.

Breakage.

A platina wire, 0·0209 line in radius and 10 lines long, was laid in the discharger and exposed to increasing discharges.

* Poggendorff's *Annalen*, vol. xlv. p. 23.

Exp. 26.—

Number of jars.	Quantity of electricity.	
4*	9	The wire is just incandescent.
	10	... is red-hot.
	11	... is at an intense white heat.
	12	... is broken in the middle.

Another wire of the same dimensions.

Number of jars.	Quantity of electricity.	
4*	12	The wire is intensely white-hot.
	12½	A piece of wire $\frac{3}{4}'''$ long remains fixed to the inner clamp (that which is connected with the interior of the battery). The remaining portion is broken into three pieces.

Exp. 27.—A platina wire, 16 lines long and 0·0261 in radius, gave the following phænomena:—

Number of jars.	Quantity of electricity.	
4	12	The wire is incandescent.
	14	... is intensely incandescent.
	15	... is white-hot.
	16	... is broken into three hooked pieces.

Similar experiments gave like results. Platina wires were made incandescent by the discharge of a certain quantity of electricity through them, and were then, by an increased quantity, while hot, forcibly torn from their fastenings. This breakage occurs oftener near to the fastenings than at a distance; the remaining portions of wire which project from the clamps are generally short, and sometimes there are none at all. The aspect of the ends of the broken wires shows that what takes place is simple breakage and not fusion, in confirmation of which further proof will be given below.

I will here incidentally correct some erroneous statements of former observers. When the intense incandescence produced by discharge in a wire is observed, it appears as if the violent heat commenced at one end of the wire and proceeded thence to the other end. Cavallo* asserts that this begins always at the positive end of the wire (that connected with the positively charged

* Treatise of Electricity, London, 1795, vol. i. p. 311.

coating of the battery) and progresses to the negative end, and he sees in this an ocular demonstration of the theory that electricity is a material substance. My attention was attracted to the fact before I had seen that statement; I observed however, with only one exception, exactly the reverse to take place, namely, that the incandescence proceeded from the negatively charged (outer) coating of the battery towards the positive (inner) coating. In order to remove all doubt that an ocular deception was effected by the position of the apparatus, I charged a battery with positive electricity, and observed clearly the progressive incandescence of the wire from the outer towards the inner side of the wire, and exactly the same when I charged the battery with negative electricity.

Van Marum * pretends to have found, that whenever a wire is partially destroyed (he ascribes it in all cases to fusion) always that part is affected which is nearest to the positive coating of the battery, the remaining whole portion being in connexion with the negative coating; and he also explains this by the assumption of an electrical materia. I found however, with a battery charged positively, that sometimes the wires were broken off at the outer and sometimes at the inner side, so that it appeared indifferent whether the positive or negative clamp retained the remaining portion of wire.

From the experiments related at page 454, it follows that the quantity of electricity necessary to break asunder a platina wire is considerably greater than that which suffices to produce the first appearance of incandescence. This quantity of electricity must also be increased if the wire is to be broken on the first discharge; for a platina wire which has already passed through several grades of incandescence is broken by a discharge which would only produce an intense white heat in a new wire. In addition to this, all wires used for experiments on incandescence must lie slack in the connecting circuit, as wires tightly stretched will often be broken by discharges of small quantities of electricity before incandescence occurs, as was mentioned above at page 439.

Wires also of other metals, which are made incandescent by the discharge of a certain quantity of electricity through them, are broken away from their fastenings by a larger quantity: but the exact quantity of electricity to be added to that which already produces incandescence, in order that this effect may take place,

* *Beschreibung einer grossen Electrisirmaschine,* Erste Fortsetzung, p. 11.

varies with the kind of metal of which the wire is composed. Although with platina and palladium the quantity has been found to be considerable, with copper it is found to be less, with silver and iron still less, and with brass and German silver extremely small. With wires of the two last-named metals it therefore frequently happens that the quantity of electricity which produces in them the first distinct appearance of incandescence, upon being discharged a second time through the wire causes them to break. Even with new wires of brass and German silver, when the quantity of electricity discharged through them was increased $\frac{1}{28}$, instead of producing the first signs of incandescence it broke them asunder.

The shivering to pieces.

If wires are exposed to stronger discharges than such as are necessary to break them, a flash of light appears, and they are shivered into a greater or lesser number of pieces, which are scattered about to some distance. It is perceptible on the examination of the collected fragments that the division of the wire into small pieces is caused by a slitting and shivering action, and that fusion, where it has taken place, is a secondary phænomenon. I shall select from my experiments upon this subject chiefly those from which the pieces of wire have been preserved, and can therefore be subjected to further examination.

Experiment 28.—A platina wire, 0·076 line thick, 16 lines long, was surrounded by a glass tube 7½ lines in diameter and fixed in the connecting circuit. The discharge of the quantity of electricity 22 contained in seven jars, just produced incandescence in the wire; the quantity of electricity 35 scattered it in pieces, which were found in the glass tube. These fragments bore evident marks of fusion on their surfaces, and four of the largest of them appeared soldered together, forming an entangled figure, which led to the supposition that they must, whilst hot, have been forcibly ejected against each other and against the sides of the tube. But the ends of all the pieces were not fused; at first sight most of them appeared sharply pointed. A tolerably straight fragment was placed under the microscope; its surface appeared uneven. On measuring its diameter with the screw-micrometer, it was found in the middle to be 0·081 line,

0·083 ...
at one end 0·022 ...
0·029 ...

This piece of wire had therefore been rent asunder lengthways. The same was observed on the piece of wire about 1 line in length, which had been left in the inner clamp. Its diameter at different parts, measured from the clamp toward the point, was

0·059 line.
0·013 ...
0·009 ...
0·005 ...

Experiment 29.—A platina wire, 0·042 line thick, was made incandescent by the quantity of electricity 8 contained in 3* jars, and was shivered to pieces by the quantity 12. A riband-like piece was at one end evidently torn off lengthways. Under the microscope, the thickest part of this end was found to be 0·043, and the thinnest part 0·018 line in thickness. A wire of the same thickness, which was shivered by the quantity of electricity $12\frac{1}{2}$, contained in 4* jars, yielded a piece, one end of which appeared jagged. We have here therefore proofs of the splintering of wires in the direction of their axes, which is quite incompatible with the assumption of a partial melting of the wires, by aid of which Van Marum endeavoured to explain the falling to pieces of the wires †. Even the superficial melting which occasionally takes place, can be altogether avoided by a careful increase in the amount of charge.

The following experiments were made with wires placed in the middle of a bell-glass 7 inches high and $5\frac{3}{4}$ inches wide.

Experiment 30.—A platina wire, 19 lines long, radius 0·0258, was made incandescent by the quantity of electricity 12 from 5 jars. The quantity 17 split it into a number of small pieces, on which no trace of fusion could be observed.

Experiment 31.—A copper wire, 18 lines long, radius 0·0253, was incandescent with the quantity of electricity 23 from 5 jars. With the quantity 27 it was torn short off from the outer clamp, and at several lines distance from the inner clamp, and converted into pieces which partly showed the bends produced by former discharges.

Experiment 32.—A silver wire, 17 lines long, radius 0·0264, was made incandescent by the quantity of electricity 22. With the quantity 24 it was torn short off from the inner clamp and split into pieces, on the outer clamp a piece about a line in length remained.

† *Beschreibung*, u. s. w. Erste Fortsetzung, S. 12.

Metals which melt before they become incandescent are also shivered in pieces by electricity before a red heat is attained. A tin wire 18 lines long was split into small pieces by the quantity of electricity 10 contained in 5 jars. The following experiment affords also an instance of this.

Experiment 33.—A cadmium wire, 20 lines long, radius 0·0394, broke with the quantity of electricity 12 from 5 jars, and was split into tolerably straight pieces by the quantity 15, which showed no signs of fusion.

The Fusion.

By constant discharges increasing in power, the wires are split into smaller and smaller fragments, which melt at the ends and on their surfaces, and at last fuse into globules. The wires are always torn away close to their fastenings and the fragments propelled to a distance. It is not difficult to determine the first stage of fusion, and to show with the same wire the fusion and splitting to pieces at the same time. All the following experiments were made under the bell-glass, and the scattered pieces of wire collected on a sheet of paper placed under it.

Experiment 34.—A platina wire of 0·0264 radius and 19 lines in length, was made incandescent by the application of the number of jars $s=5$ and the quantity of electricity $q=11$; the quantity of electricity 20 split and melted it. Many of the fragments, about half a line in length, had small globules on their ends, and besides these there were some single globules and unmelted splinters of wire.

Experiment 35.—A silver wire (radius 0·0264, length 15 lines) was split and melted when $s = 6$ and $q = 26$. Besides single globules, bent fragments were collected with splinters melted upon them.

Experiment 36.—A tin wire (radius $0^{m}{\cdot}037$, length 20 lines) was torn from its fastenings by a discharge in which $s = 6$ and $q = 8$; another wire was split into pieces by the quantity of electricity 15, and left evidently melted pieces behind in the clamps.

When a larger quantity of electricity was employed (24) melted globules dropped from the wire, which sprung about red-hot in the usual manner whilst oxidizing.

Complete fusion of the wires was obtained in the following experiments.

Experiment 37.—A platina wire of the same dimensions as that used in Exp. 34, was melted into a number of small perfectly round globules by a discharge in which $s=5$, $q=22$.

Experiment 38.—A silver wire (radius 0·0264, length 19 lines) was melted into globules when $s=6$, $q=26$.

Experiment 39.—A copper wire (radius 0·0253, length 16 lines) became incandescent when $s=6$, $q=25$, and was converted into a multitude of very minute globules by a discharge in which $q=30$. The globules were some of them so small as only to be perceptible with the magnifier. I made several unsuccessful attempts to obtain larger globules of copper.

It may appear striking in these experiments, that the charge necessary to produce complete fusion is not much greater than that which causes the first appearance of incandescence in the wire. In oxidizable metals the temperature is increased by the absorption of oxygen from the air, and a chemical effect is thus added to the electrical. This is most remarkably shown in the case of iron, which often is melted by discharges, which in themselves would only have produced a moderate incandescence. But the kind of fusion is then peculiar, as the following experiments show.

Experiment 40.—An iron wire of $0'''·0266$ radius and $17'''$ long, which when $s=3$ and $q=10$ would have shown the first signs of incandescence, became intensely red-hot on the discharge of the quantity of electricity 13. The incandescence did not cease immediately, as on all other occasions, but was increased to a white heat; a few globules dropped from the wire and sprung about on the table, emitting vivid scintillations. The ends of the wire, some lines in length, which remained in the clamps, were melted into globules, and retained the position which they had before the commencement of the experiment.

The iron wire is quite differently affected by more powerful discharges, even when these are insufficient to produce perfect fusion.

Experiment 41.—An iron wire of 0·04 line radius, 16 lines in length, was brought to incandescence when $s=7$ and $q=25$. When $q=30$ it was broken to pieces whilst red-hot, and was fused, so that three globules, which were oxidized while springing about, and three pieces were collected. The long wire-ends which remained in the clamps were forcibly bent round them; and on one end a globule was melted. We know that thin iron

wires, when taken red-hot from the fire, if they have not been previously oxidized on the surface, will become heated until they melt, and that melted copper by the absorption of oxygen is converted into a pulverulent state. The experiments described above show that the fusion of these two metals by means of electricity is materially affected by the absorption of oxygen, and that probably the same takes place with the other metals. This is confirmed by the fact established by different observers, that even platina is fused much more readily by electricity in the open air than in an exhausted vessel.

Electrical fusion is a very complicated phænomenon, and it is impossible to arrange the metals in the order of the powers of the current of discharge necessary to produce their fusion, because the same amount of fusion cannot be attained in each metal. Silver, and particularly copper, is only to be obtained in fine globules; brass and German silver cannot be obtained in globules at all. We could therefore only take as a standard the size of the fused portions, which is dependent upon many contingencies. In general it must be borne in mind that in all the metals fusion takes place after the shivering to pieces, and that in those metals which become incandescent without melting the shivering to pieces occurs after the first appearance of visible incandescence by daylight. For this last phænomenon the laws have been developed above.

Residue of Charge after Fusion.

Van Marum* remarked, that a certain charge of the battery was necessary to melt a given length of wire, but that only a part of the accumulated quantity of electricity was consumed in producing fusion; that portion which remained behind in the battery being considerably larger than was usual on other occasions.

I have endeavoured in the following experiments to determine the amount of this residuary portion: the experiments were made with the battery used in the beginning.

Experiment 42.—A platina wire (radius 0·02089, length 15 lines) was fixed in the connecting circuit, and when it had been destroyed it was replaced by a precisely similar one. On the discharge of different quantities of electricity the following appearances were observed:—

* Beschreibung, &c. Erste Fortsetzung, p. 13.

Number of jars.	Quantity of electricity.	
5*	12	The wire is brightly incandescent.
	14	Distorted—broken off.
	15	Torn into three pieces.
	17	Melted into globules.

(The battery was insulated immediately after the discharge.)

	12	The wire is shivered to pieces.

After this preliminary experiment, the quantity of electricity could be so chosen that in the one wire first incandescence and then fusion, in the other immediate fusion should take place; and as the battery was insulated immediately after the destruction of the first wire, the quantity of electricity retained in it could be made to assist in the fusion of the second wire. In order to shorten the time between the two fusions, both the wires were fixed in one of the clamps at the same time, whilst into the other clamp first the end of the one wire was introduced and then the end of the second.

Experiment 43.—

Number of jars.	Quantity of electricity.	
5*	13	The first wire is brightly incandescent.
	17	It is melted into globules.
	13	The second wire is melted into globules.

This experiment was repeated twice with the same result.

For the complete fusion of these wires, the quantity of electricity 17 was therefore necessary; as after the first fusion the addition of the quantity 13 sufficed to produce this effect, there must have remained in the battery after the first fusion the quantity of electricity 4, or nearly 0·23 of the whole charge. This residue appears very large, even when notice is not taken of the fact, that the discharge took place through a perfect metallic connexion of the two surfaces. When the discharge was made at the principal discharging distance, in which case the connecting circuit was interrupted by a stratum of air, this battery retained, as I discovered by former experiments*, only $\frac{9}{13}$, or 0·15 of the whole quantity of electricity. The considerably greater residue in the present case shows therefore that the continuity of the platina wire must have been destroyed before complete discharge at that distance could occur, and that this destruction of continuity must therefore have taken place in a

* Poggendorff's *Annalen*, vol. liii. p. 11.

remarkably short space of time, and indeed upon the first partial discharges. This affords a new confirmation of what I have endeavoured to establish, that the electrical fusion of the metals is not due to a gradual increase of temperature, but must be attributed to a more quickly acting mechanical agency.

The Reduction to Powder.

The first visible direct action of the electrical discharge upon a new wire consists, as was remarked at page 437, in the formation of a cloud of vapour or smoke rising from the wire. It is probable that this vapour is composed of metallic particles forcibly separated from the surface of the wire, and dependent therefore in quantity upon the nature of the surface. By increasing the power of the discharge beyond what would be required to melt the wire completely, we are enabled to convert the whole mass of wire into vapour. This conversion is accompanied by a brilliant display of light and a loud report.

Experiment 44.—Through a platina wire, radius 0·0209, length 15 lines, enclosed in a glass tube, which was made incandescent by a discharge in which $s = 5$ and $q = 13$, and was melted into globules when $q = 17$, the quantity of electricity 22 was discharged. It disappeared with a brilliant light, and the tube was covered with a gray sublimate, which could be wiped off.

The experiment was repeated in the air and a plate of mica fixed horizontally a few lines above the wire. The vapour into which the wire was converted covered the mica with grayish and blackish spots, which under the microscope, with a power of 280, appeared to consist of metallic fragments of different sizes and shapes. Comparatively there were but few melted particles and globules.

The dispersion of the wire evidently consisted in its reduction to powder, in a mechanical separation of the metal into small particles. All the metals can thus be reduced to powder, but the power of discharge requisite to produce this effect stands in no relation to that which is required to melt the metals. Thus tin is melted by a less powerful discharge than cadmium, but the discharge which completely reduced the latter metal to powder left the greater part of the tin in a fused state. The brittleness of the metal has evidently the greatest influence on its reduction to powder.

Finely-divided metal, many of the particles of which are heated

to the melting-point, is thus placed in very favourable circumstances for the absorption of oxygen and for its conversion into oxide. If metal therefore is reduced to powder by electricity exposed to the air, the greater part of it is found converted into oxide. At the time that the first careful experiments of this kind were instituted, Lavoisier's theory of oxidation still admitted of controversy, and we find therefore that the greater number of those experiments were applied, as experiments on oxidation, to the solution of chemical problems, which now have no longer any interest*. Van Marum demonstrated the existence of metallic oxides, by reducing to powder metallic wires placed about one-eighth of an inch above sheets of paper, which latter were variously coloured by them. I prepared a few such figures with imperfect access of air, by confining the wires between two pieces of paper and pressing them together with a pound weight. In this manner, besides the colours produced by the oxides, pure metal was visible. It was particularly distinct with copper and cadmium, where between dark-coloured ramifications metallic veins were entangled, distinctly perceptible by their colour and lustre. It is, however, well-known that in irrespirable gases, and *in vacuo*, the powder to which the metals are reduced by electricity is also metallic†. Thus the opinion is distinctly controverted, that the metals are oxidized by means of electricity, and their oxides scattered as powder.

Mechanism of Incandescence and Fusion by Electricity.

Mechanism of Fusion.

The marked effects produced by increasing discharges of electricity upon metallic wires may be arranged, beginning with the weakest discharge, in the following order: the wire becomes warm; is violently shaken; bends are produced in it; it is made incandescent; torn away from its fastenings; split into pieces; melts; and is converted into powder. The mechanical and calorific effects alternate here with each other, but they often

* Van Marum, *Beschreibung*. Erste Forts. p. 13. Cuthbertson, Nicholson's Journal, v. p. 136. Gilbert's *Annalen*, vol. ii. p. 400. Singer, *Elemente der Elektricitätslehre*, Breslau, 1819, p. 122.

† Guyton-Morveau, Gilbert's *Annalen*, vol. xxxii. p. 55. Van Marum, *Beschreibung*. Erste Fortsetzung, p. 26.

occur simultaneously. No incandescence takes place in the wire without a bend becoming observable in it, and it is seldom that fusion is effected without traces of splitting in the wire. The first action in this series is the only one in which heat alone is concerned; if it concurs in the production of any of the following effects, then the calorific and mechanical action must both equally be taken into consideration.

As far as the fusion is concerned, the detailed experiments point out so clearly what then takes place, that it will only be necessary here to add a very few words.

We have seen, that by means of increasing discharges, a wire is forcibly torn into splinters, which show no trace of fusion, that it is then shivered into partially fused splinters, and, lastly, is melted into globules. Even in this last case the splintering effect is visible from the force with which the globules are scattered about. If a greater mass of metal is only partially melted on the surface, the never-failing formation of vapour shows the mechanical action which accompanies fusion; it is not the small particles of metal forcibly thrown off that suffer fusion, but these enable the remaining portion of metal to melt by loosening and lacerating its surface. Wherever electrical fusion takes place a mechanical separation of the melted mass is visible; the fusion can therefore only be considered as the effect of heat upon finely-divided metal. When fire acts upon a metal, it heats continuously the whole cohering mass until it melts; electricity, on the contrary, only heats a metal to temperatures below the melting-point, and fuses it by simultaneous splitting to pieces and heating. This then is the essential difference between fusion by fire and by electricity, which led Franklin and Berthollet to the opinion mentioned in the introduction, according to which electricity was supposed to dissolve the cohesion of a metal without the aid of heat. That opinion, however, was so far erroneous, as no notice was taken of the development of heat which accompanies every electrical discharge long before its mechanical powers are exerted, and the facility with which the minute particles of metal, when reduced to powder, are oxidized, is clearly due to the agency of heat. The mechanism of electrical fusion is distinguished from that of ordinary fusion when thus expressed: *Electricity fuses a metal by simultaneously splitting it in pieces and heating it.*

Mechanism of Incandescence.

Incandescence also is not to be included amongst the mere calorific phænomena of electricity; the mechanical effects which precede it, the formation of vapour, the vibrations, and more particularly the constant bends produced in the wire, prove this in a direct manner. Indirectly we arrive at the same conclusion from the facts, that the increase of temperature produced by altering the connecting circuit and the charge, the laws of which for low temperatures are known, is insufficient to enable us to calculate the temperature of incandescence (p. 434), and that, from the power of the current which produces incandescence in one metal, we cannot calculate the power required to produce incandescence in another metal. With wires of the same metal, differing only in their dimensions, the dependence of incandescence upon the power of the current was found exactly to correspond with what might be determined by the established laws regulating the excitation of heat in different wires. Like temperatures in different measured wires presuppose the same relations of temperature in a constant wire, as were here really found for the incandescence. The variation from the course of the regular temperatures is here also perceptible, if the thermometrical changes in a constant connecting circuit, with different discharges, are compared with each other. For a constant circuit in which no part suffers mechanical action by the discharge, the thermometrical alteration θ, on the discharge of the quantity of electricity q contained in s jars, is expressed by the equation $\theta = \alpha \frac{q^2}{s}$, in which α remains so distinctly constant throughout a whole series of observations, that, as was the case in all my researches on heat, one value for α is sufficient to establish the whole series. This is no longer the case when a wire is included in the connecting circuit, which is mechanically affected, and is made incandescent by the discharge employed. The value of α decreases considerably from the first mechanical action upon the wire until it becomes incandescent, remains during the different grades of incandescence nearly constant, and again increases on the wire being split in pieces and fused. This is obvious from the following experiments.

Experiment 45.—A platina wire, 16 lines long, radius 0·0261,

was placed by the side of the thermometer in the connecting circuit.

Number of jars.	Quantity of electricity.	Indication of thermometer.		
s.	*q.*	*θ.*	*α.*	
4	6	12·5	1·39	
	8	20·7	1·29	Vapour over the wire.
	9	23·8	1·17	The same.
	10	27·2	1·09	Bend in wire.
	11	31·0	1·02	The same.
	12	36·0	1·00	The same.
	13	42·5	1·00	Wire is incandescent.
	...	41·8	0·99	The same.

Experiment 46.—A platina wire, 16 lines long, radius 0·0396, was placed by the side of a less sensitive thermometer.

Number of jars.	Quantity of electricity.	Indication of thermometer.		
s.	*q.*	*θ.*	*α.*	
7	10	8·0	0·56	
	12	9·3	0·45	
	14	11·8	0·42	
	16	13·5	0·37	
	20	19·8	0·35	
	22	24·9	0·36	Wire is incandescent.
	24	26·7	0·33	The same.
	26	31·8	0·33	The same.
	28	32·6	0·29	The same.
	35	45·0	0·33	The wire is melted.

Experiment 47.—A platina wire 17 lines long, radius 0·0209.

Number of jars.	Quantity of electricity.	Indication of thermometer.		
s.	*q.*	*θ.*	*α.*	
Old battery.				
4*	5	7·6	1·22	
	7	14·0	1·15	
	9	20·0	0·99	Wire is bent.
	11	27·2	0·90	Wire is incandescent.
	13	33·3	0·80	Wire is white-hot.
	15	41·2	0·95	Wire is melted into globules.

Experiment 48.—A wire of the same thickness, 10 lines long.

Number of jars. s.	Quantity of electricity. q.	Indication of thermometer. θ.	α.	
4*	5	7·8	1·24	
	6	9·0	1·00	
	7	12·8	1·04	A bend in the wire.
	9	17·5	0·87	The same.
	10	20·6	0·82	Wire is incandescent.
	11	24·0	0·79	The same.
	12	27·1	0·75	The wire is white-hot.
	$12\frac{1}{2}$	28·0	0·93	The wire is broken to pieces.

In those cases where destruction of the wire ensued, the value of α is calculated, not for the whole quantity of electricity q, but for 0·77 q, retaining the whole amount of intensity, as nearly 0·23 of the whole quantity used remains behind in the battery (p. 461).

If the retarding power of the thin wire in the connecting circuit is expressed by V, then former researches show that the magnitude of α is proportional to $\frac{1}{1 + b\,V}$, in which the value of b is dependent upon the constant part of the connecting circuit. The visible decrease of the value of α in the above experiments, which with the discharges employed only happened when the thin wire was used, indicates therefore an increase in the retarding power of this wire. Beginning with the discharge which produced the first mechanical effects, the wire obstructs the following discharges so much the more the stronger they are. But these retardations do not keep even pace with the increase of the discharge; certain periods are observed, within which they vary but little, and these periods are in evident connexion with the effects of the discharge. Thus the first considerable increase of retarding power occurs when the wire is violently shaken by the discharge, the second with the appearance of bends in the wire, and when the wire at length fuses the retarding power again decreases. Thus the first conjecture which presented itself is contradicted, that the retarding power of a wire is dependent upon the temperature which the wire acquires by the discharge (in which case the discharge must be considered as dissected into the different pulsations, of which it is composed).

The retarding power of a wire is therefore solely dependent upon the manner in which the discharge progresses through it; its mutability up to a certain point, and subsequent continual alteration until the wire is destroyed, shows therefore that in every wire weak discharges are propagated in a different manner than strong ones. I shall endeavour in the sequel to explain hypothetically the nature of this different manner of propagation, and as the propagation of more powerful discharges produces the mechanical and calorific effects spoken of in this treatise, I shall at the same time endeavour to assign a reason for these effects. The mechanism of incandescence may be thus expressed: *The incandescence of a wire is produced by a propagation of the electrical discharge through it, in a manner quite distinct from that which causes the wire to become heated.*

On the different Modes of Propagation of the Electrical Discharge.

Different Modes of Propagation in Metallic Wires.

Whatever view is taken of the nature of electricity and of electrical conduction, we are forced to assume that in the metals the electrical state is communicated successively from one molecule to the next. If therefore a piece of metal is electrified at one part, it can only be brought back again to an unelectrified condition after every particle has become first electrified and then unelectrified. In some cases two points are discernible in every part of the piece of metal which chronologically assume these two states one after the other; the straight line uniting these two points is then called the line of propagation of the electricity. A battery discharged by a homogeneous cylindrical wire affords such an instance. The discharge is effected by the wire connecting the two coatings becoming in a series of successive pulsations first electrified and then unelectrified, and in every part of the wire that end which is nearest to the inner coating of the battery must become by the electricity of that coating sooner electrified than the more distant end; all the parts however which lie in a normal section of the wire must be simultaneously electrified and simultaneously unelectrified. The discharge of an electrical battery must therefore be considered to take place by the progression of a certain electrical state from one section of the homogeneous connecting wire to the next im-

mediately following it; and further, this progression must take place equably, so that in every part of the wire the same number of sections become electrified in the same interval of time. The laws of the electrical excitation of heat support this view in the most distinct manner. We will call the discharge of the battery taking place in this manner the constant or *continuous* discharge. But suppose that at one molecule of the connecting wire the electrical state is in some manner prevented from communicating itself to the next contiguous molecule, the continuous discharge can then no longer take place. That molecule will become much more strongly electrified than it would have been by the continuous discharge, and its electricity will continue to increase in intensity until it is enabled to overcome the obstruction offered to it, and thus bring itself into equilibrium with the electricity of another molecule. The molecules thus being brought into electrical equilibrium are no longer in intimate contact, but are at a measurable distance from each other. Thus a totally different mode of discharge is here concerned, from that which we previously examined. It is no longer imperatively necessary that all the particles of a normal section of the wire should be in the same electrical state at the same time; the direction of the discharge is no longer necessarily in the same line with the axis of the wire, but may form any angle with it. As also a certain time elapses before the first particle acquires sufficient electric tension, and during that time the progression of the discharge is retarded, therefore the discharge will not be propagated in the same space of time through wires of equal length. It may happen, that whilst in one part of the wire this propagation of the discharge by starts or jerks is taking place, in another part continuous propagation may be going on; but the discharge of the battery can then no longer be completed in a constant manner, and we must designate this mode as the intermittent or *discontinuous* discharge. The effects which a discontinuous discharge exerts upon a connecting wire may be deduced from known experiments, in which this mode of discharge by a discontinuous connexion of the battery was artificially effected. Phænomena of light, fusion and mechanical action occur. A chain of links, through which discharge was made, became luminous, metallic powder was evolved from it, the links were forced from their positions, and some of them melted together. A string of metallic beads was torn in pieces

by the discharge; the beads were scattered and melted on their surfaces*. If a moderate battery discharge is passed through a thin strip of tin foil, no visible alteration is produced in it. If the strip is attached to a plate of glass and cut through in different places, and the ends of each piece slightly loosened from the glass, then, by a similar discharge, the ends will be lifted up and bent back, so that each acquires the form of a c turned on its back (ɔ)†.

The discontinuous discharge artificially produced causes therefore the same effects as were observed above in wires which had been submitted to discharges exceeding a certain strength. The luminous appearance which accompanies every artificial intermittent discharge, occurs also, though seldom, when discharges are passed through thin wires. Van Marum describes an instance‡, in which an iron wire that was made incandescent by a discharge was at the same time surrounded by a brilliant light, which appeared to be about an inch in diameter. Here the discharge must have taken place at those points where it was intermittent, partly through the substance of the metal and partly by spreading itself over its surface. Not only do the striking external phænomena of the wire oblige us to assume a naturally caused discontinuous discharge, but the less obvious effects in the wire are more easily explained by such an assumption.

It has been shown, that with the first mechanical action upon the wire its retarding power was increased; as the discharge then becomes intermittent, its transmission through the wire must require a longer time. The points of intermittence of the discharge are indicated by the bends; the more these increase in number the greater is the retarding power of the wires. But at the same time this is lessened by the discharge springing from place to place, which occurring at so short a distance carries forward the discharge more quickly than would happen by a continuous discharge; this accounts for the periods in which the retarding power remains nearly constant, and for its decrease on the splitting to pieces and fusion of the wire. This compensation of the two opposite actions is illustrated by a case which I published on a former occasion §. In the connecting wire of

* Priestley, History of Electricity, German edition, by Krünitz, p. 440.
† Henry, in Transactions of the American Philosophical Society, vol. vi.
‡ *Beschreibung einer Elektrisirmaschine*, Zweite Fortsetzung, p. 48.
§ Poggendorff's *Annalen*, vol. xliii. p. 78.

a battery, close to an air thermometer, an interruption of the circuit was made and two small plates of brass introduced parallel and opposite to each other. The plates were first placed at one-tenth of a line and then at one line apart from each other. Similar discharges produced an increase of temperature in the thermometer, for the most part not less and sometimes greater in the latter position of the plates than in the former. Although in the more distant plates the discharge took place with a less quantity of electricity than when they were placed nearer to each other, the more complete condensation of the electricity on the edges of the plates completely compensated the diminished effect upon the temperature from the former cause.

After what has been stated, the discontinuous discharge of large quantities of electricity through continuous wires can no longer be doubted. The partial fusion of the wires, the common occurrence of their splitting to pieces in the direction of their axis, and the remarkable bends which appear previous to incandescence, afford clear additional proof of this manner of discharge; whilst, on the other hand, with smaller quantities of electricity, the like increase of temperature in every similar segment of the wire most indisputably establishes the continuous propagation of the discharge. To present a clear idea of the action of an electrical discharge upon a wire, we must therefore express ourselves in the following manner:—

Electrical discharges, up to a certain degree of intensity, are propagated continuously through every wire; causing the wire to become warm and magnetic; more powerful discharges propagate themselves through the wire only in a discontinuous manner, the results of which are the bends, incandescence, the tearing to pieces, the fusion and reduction to powder of the wire.

Different Modes of Propagation of the Discharge in Fluids.

The different modes of propagation of the electrical discharge in one and the same medium are by no means confined to the metals; they are so striking in imperfect conductors of electricity that they could not be overlooked. Faraday * adopts four different modes of electrical discharge through the air, which he distinguishes by their attendant luminous appearances and mechanical effects,

* Experimental Researches in Electricity, London, 1839.

and designates, disruptive discharge, glow discharge, dark discharge, and carrying discharge. These discharges belong essentially to the discontinuous kind of discharge; whilst the gradual dispersion of electricity into the air, established by the laws of Coulomb, must be considered as the continuous discharge of an electrified body through the substance of the air. The different modes of propagation of discharges through fluids are no less evident. A battery can be discharged completely and without the least noise through a tube filled with water, alcohol, or some saline solution; but by slightly increasing the power of the discharge, a spark is seen to pass in the tube and it is forcibly shattered to pieces. Fluids are decomposed into their component parts by a noiseless discharge, and these appear singly at certain points which may be at any distance from each other; whilst the explosive discharge leaves the component parts of the scattered fluid everywhere in a combined state. Although these effects of not very different quantities of electricity sufficiently prove the different modes of propagation, still I have further shown them to exist by observations on a thermometer placed at the same time with an imperfect conductor in the connecting circuit. A moist piece of wood, $1\frac{1}{2}$ line in thickness, was clamped between two points in the connecting circuit, or a damp card was used to connect two points at 10 lines distance from each other; the discharges up to a certain intensity passed through without noise, and the thermometer did not show the least signs of being heated. But at a certain point, when the discharge was only slightly increased, it pierced the interposed substance with an emission of light and a violent report, and raised the temperature of the thermometer considerably. In these experiments however the battery was only in the last case completely discharged, whilst in the former no inconsiderable quantity of the electricity remained behind. I shall therefore only call attention to the following more accurate experiments, in all of which a complete discharge of the battery was effected.

Experiment 49.—At an interruption in the connecting circuit two platina wires, 0·224 line in thickness, were placed perpendicularly and bent at an angle, so that their points were at $\frac{1}{3}$ line distance from each other: they were thus immersed in a vessel of distilled water. A thermometer placed in another part of the circuit indicated on the different discharges the following temperatures:—

Number of jars.	Quantity of electricity.	Rise in temperature of thermometer.	
4*	5	0	
	$5\frac{1}{2}$	0	
	6	0	
	$6\frac{1}{2}$	27·5	
	7	35·0	32
3*	4	0	
	$4\frac{1}{2}$	0	
	5	19·0	22·4
	$5\frac{1}{2}$	32·3	27·5

As the increase of temperature in the thermometer depends upon the mode in which the electricity is propagated through the water, the indications above show two modes of propagation. If the quantity of electricity 6 had been propagated through the water in the first experiment in the same manner as the quantity $6\frac{1}{2}$, then a rise in the thermometer of 23 lines must have occurred; in the second example, the quantity $4\frac{1}{2}$, if propagated in the same manner as the quantity 5, must have produced a rise of 15·5 lines in the thermometer. Instead of these two quantities no appreciable change was observed. The discontinuous discharge was also evinced by a hollow sound, attended by a spark, in the water, which latter was scattered about. If the experiment is made with a greater distance between the platina points, and a consequently greater quantity of electricity, the vessel containing the water is often shattered in pieces.

Position of the Points of Intermittence in Wires.

The slightly varying elevations of temperature obtained in forty-nine experiments, with the same discharges, should not surprise us; for we may easily suppose that in breaking through a fluid mass the discontinuous discharge is not always obliged to take the same course. This applies with like force to solid bodies, and especially to the metals when they are broken through and split into pieces. Wherever, on the contrary, the discharge is insufficient to dissolve the cohesion of the metal, it takes place more regularly, and seizes simultaneously the normal sections of the wire, as the uniformity of the thermometrical changes on the incandescence of the wire and the dependence of these upon the diameters of the wire clearly show. We may now inquire concerning the position of the points of intermittence. A

charge of a certain strength cannot be propagated continuously through a wire of certain definite dimensions; it must be once or more than once intermitted. The points at which this intermittence occurs, and which are hypothetically pointed out by the bends, appear to be arbitrary, and only occasioned by casual inequalities in the substance of the wire. If for an experiment upon incandescence a wire is chosen which at some point has been squeezed or indented, in spite of the most careful straightening and smoothing, the first bend is sure to occur at that point. It is easy to produce a distinct bend at any part of the wire previously fixed upon. I have often indented a wire at a certain point with the nail of my finger, and always found that the first bend caused by the discharge took place at that point, whilst all the other phænomena in the connecting circuit remained unaltered.

The Electric Spark.

The present inquiry is connected with the question so repeatedly raised concerning the nature of the electric spark, and in conclusion I will offer a few observations respecting it. If a sufficiently strong charge is passed through a good conductor and an imperfectly conducting liquid or gas, the discharge becomes intermittent in the latter medium, and a luminous appearance is produced, an electrical spark, or some modification of it. Concerning the nature of this spark two essentially different opinions are entertained. According to the one, the medium itself (generally the air) through which the discharge passes becomes luminous by a primary or secondary action of electricity. To this view an analogy is found in the above experiments, where it has been shown that a metallic wire becomes incandescent by an intermittent discharge, its substance therefore becoming luminous. The other opinion supposes the spark to consist, not of luminous particles of the medium itself, which it traverses, but of incandescent particles of the good conductors which border that medium, and which therefore generally consist of red-hot metallic particles. This view is also not contradicted by the above experiments. It is easily shown that the discontinuous discharge does not only take place in the imperfect conductor, but begins at a slight depth in the good conductor. If a spark be taken from a metallic conductor, the intermittent discharge is indicated by the pricking sensation in the finger; or if a piece

of metal be used, and the experiment frequently repeated, by the oxidation of its surface. The discharge of a battery produces in the first experiment oxidation and fusion in the balls between which the spark passes. The discontinuous discharge has also, as we have seen, the effect of detaching and fusing particles of metal; and when pieces of metal are used, the presence of metallic particles in the spark is quite intelligible. This however by no means proves the necessity for such particles in every electric spark, and the opinion concerning the nature of the electric spark which is founded upon these facts, although supported from different quarters in modern times, offers so many difficulties, that its complete establishment can only be effected by more extended researches than have hitherto been made.

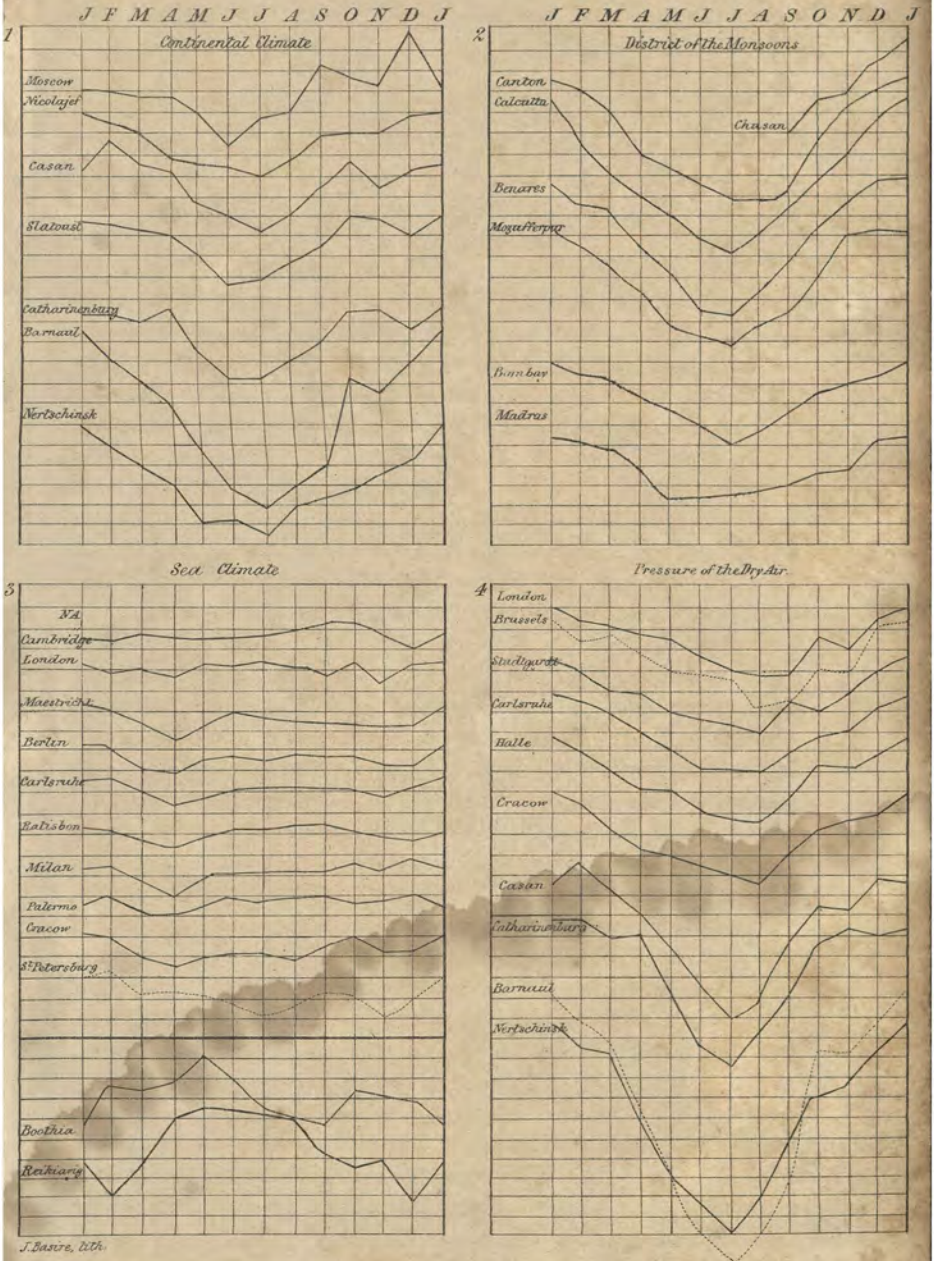
Article XVI.

On the Periodical Variations in the Pressure of the Atmosphere in the Interior of Continents. *By Prof.* H. W. Dove.

[Read before the Royal Academy of Berlin, October 1842.]

METEOROLOGICAL phænomena appear under such a variety of forms in the different parts of the earth, that the theories advanced for their explanation bear more or less the stamp of the locality in which we are accustomed to observe. The annual periodical cycle is likewise of such great importance in this inquiry, that what the traveller gains by changing his place of observation is partly lost by not passing such a period with the atmosphere at the same locality. In avoiding therefore local errors he is apt to fall into temporal ones. Moreover, the periodical phænomenon becomes fully known only by its repetition; and it is now agreed that the science is best promoted by stationary sets of observations extending over large districts of the surface of the globe.

On the coasts of England the attention of Saussure would not have been called to the importance of the ascending current, nor would Hadley have discovered the theory of the trade-winds in the valleys of Switzerland. If therefore we admit that mountainous countries have been the birth-place of meteorology, we must, on the other hand, confess that its progress was much promoted when it descended from the mountains into the plains. The substitution of Hutton's rain theory for that of Deluc, the exchange of Saussure's hygrological ideas for those of Dalton, are striking instances of this transition. It is owing to the dissimilar conceptions of the mountaineer and of the inhabitant of the plain having obtained their full estimation in the science, that the two fundamental principles of atmospheric processes, the motion of the air in vertical and horizontal direction, have obtained equal justice. Certainly, wherever we are, we can see but one of these operations in force; and even, as Espy has done, place an ascending current as leader at the head of a whirlwind; but we have only to cast our eyes on one of Redfield and Reid's maps of storms to be convinced that such an idea is by no means in accordance with nature.



Dove on the Pressure of the Atmosphere.

But even if we no longer adhere to Saussure's partial view, —if we acknowledge that a science so nobly begun by him has not since remained stationary,—if we consider the currents of air as the true levers in general of meteorological phænomena (caused, it is true, by the vast ascending current in the regions of calms producing the trade-winds), meteorological theories may still bear the stamp of that locality, of which they have to free themselves in order to attain their real importance; for they all are written under the influence of the sea-climate. The admission of America into the circle of observations has certainly contributed essentially to correct the defective Europæan ideas respecting the distribution of temperature, but even in America the true continental relations do not occur. Only now is meteorology penetrating into the true continental climate. For its finding a place there we are indebted to Count Cancrin, who has connected the most distant provinces of the Russian empire by a net-work of observations with those stations where formerly observations were made with Manheim instruments. The careful reduction of these observations, and their quick publication by M. Kupffer, renders the results obtained common property, and admits of our starting questions which previously it was not possible to think could ever be answered.

The antithesis of continental and sea-climate is generally applied only in reference to relations of temperature, and is therefore most distinctly indicated in the distribution of vegetable forms as its most direct expression. It also explains how the drops on the surface of the water, cooled by the immediate contact with the air, sink to make room for those more warm from the deep; the alleviation of the winter's cold from the vicinity of the sea just as simply as the lowering of the summer temperature from the heat rendered latent by evaporation. But it is evident that the vapour formed, will not only at its origin influence the phænomena of temperature, but, as an elastic fluid taking a share in the general pressure of the atmosphere, must also be of importance with reference to the barometrical relations.

We are accustomed to look upon the barometrical changes as an expression more or less direct of the thermometrical. This view is founded upon the experience that in the so-called irregular changes a diminution of the atmospheric pressure is generally accompanied by an elevation of temperature; and, on

the contrary, that the air becomes cooler when the barometer is rising. But no notice is taken of the fact that in the daily period the atmospheric pressure attains two maxima and two minima, while the temperature, on the contrary, uniformly rises and falls within twenty-four hours; and that something similar is observed during the annual period, at least in Europe, where moreover the pressure during the decided summer months is much higher than in spring.

These contradictions appear to me so striking, that I attempted to remove them in two treatises published in Poggendorff's *Annalen* ten years ago. One of them, 'On the Physical Causes of the Daily Changes of the Barometer,' is printed in vol. xxii. pp. 219 and 493; the other, 'On the Distribution of Atmospheric Pressure during the Annual Period, and on Barometric Levelling of the Plains,' in vol. xxiv. p. 205. My mentioning here this circumstance again may be justified by the view then advanced having received a remarkably evident confirmation in the North Asiatic observations.

This view is, that although a separation of the vapour-atmosphere seems not to be essential in the variations of the atmospheric pressure dependent on the direction of the wind, it becomes indispensable in the explanation of the periodical variations.

The pressure of the dry air, the elasticity of the vapours, and the temperature, attain their extremes nearly at the same points of the wind-rose. Their distribution within the wind-rose is likewise so analogous, that it may be expressed by the same function of the direction of the wind. Leaving out of question the fact that the vapour-atmosphere alone will not produce a wind different to that originating at the same time in the dry air, that therefore moist atmosphere, when moved horizontally, will be moved as a whole, it is proved by empirical data, from calculated barometrical and atmospherical wind-roses, that the total pressure of the atmosphere in its changes, dependent on the direction of the wind, follows the same principles fixed by the law of rotation as the dry air. A separation therefore of the variations of the vapour-atmosphere will only be necessary with respect to the precipitates which originate from the reciprocal displacement of winds of unequal temperature. But setting aside these precipitates, the total pressure of the atmosphere in its so-called irregular variations, may be regarded as a direct

function of the temperature; however, the correctness of this assumption is evinced for the first time by the reasons now advanced.

As regards the motions of the atmosphere in vertical direction, by which the barometer is moved periodically during the day and the year, the nature of the district over which the air ascends, whether it be solid or liquid, will be of essential influence. Formerly, when we possessed only observations of the sea-climate, the first case could only be imaginarily represented by calculation; now, that we are able to avail ourselves of observations of the continental climate, the abstraction formerly obtained so completely merges in reality, that this latter almost loses the charm of novelty.

1. *Annual Variations.*

As the dry air and the aqueous vapour mixed with it press conjointly upon the barometer, the raised mercurial column consequently consists of two parts, one of which is supported by the dry air, the other by the vapour; we shall easily understand that, as with rising temperature, the air increases in volume, and consequently ascends and flows off laterally above, while, on the other hand, at a higher temperature the evaporation increases, and therefore the elasticity of the vapour contained in the air is augmented, the periodical changes of the barometer cannot stand in a very simple connexion with the periodical changes of temperature; for as long as we are unacquainted with the quantitative proportion of both these changes, which occur at the same time but in opposite direction, we cannot even decide whether the total pressure will augment or diminish with an increase of heat; whether perhaps during one portion of the period the preponderance may not be on the side of the one change, while during the remainder of the period it is on the side of the other. It is evident therefore that we can only expect to obtain a knowledge of these variations by cotemporaneous observations of the barometer and hygrometer.

What is gained by this separation will be seen by a glance at the illustrations which accompany this memoir. The figures 1, 2, 3, Plate VI. contain the variations of the total pressure during the annual period; fig. 4, the annual variations of the pressure of the dry air only. In the temperate zone the places having a continental climate are separated from those having a

sea-climate (figs. 1, 3), and this appears justified from the form of these curves being entirely different. In the illustration (fig. 4) representing the pressure of the dry air, the Europæan and Asiatic curves are, on the contrary, similar to each other, and pass so gradually into one another, that a separation would appear arbitrary. The supposition which immediately presents itself, viz. that from winter to summer the atmospheric pressure diminishes regularly as the temperature increases, is actually realized in Asia. But this decrease generally occurs in Europe only until April, the pressure then increases until autumn, and attains a second minimum in November, when it again quickly rises. That this deviation is owing to the admixture of vapour, is proved by the circumstance, that after elimination of its elasticity, a uniform increase and decrease of the atmospheric pressure, corresponding to the changes of temperature, is likewise evident in the Europæan curves of fig. 4. Consequently, what the total pressure of the atmosphere loses in Asia by the thermal rarefaction of the air, is not wholly compensated by what it gains by the increase in the elasticity of the vapour produced by the rise of temperature (fig. 4). On the coasts of the Atlantic, on the contrary, an over-compensation takes place (fig. 3), the total pressure gains more by the increase of elasticity of the vapours than it loses by the rarefaction of the air. It is on this account that in the most decided sea-climate, in Iceland, the annual curve of the atmospheric pressure has an entirely opposite form to that in the interior of Asia. Europe forms the transition from the one extreme to the other. Should it be required to trace a line of demarcation between the continental and the sea-climates, it would be where the decreasing pressure during the summer passes into an increasing one. St. Petersburg, Moscow, Nicolaieff, are on one side of this line; Wilna, Cracow, Ofen, on the other.

The application of the hypsometric formula presupposes the elimination of periodical variations of the atmospheric pressure at the stations of observation, which condition Ramond attempted to satisfy for the daily period by proposing 12 A.M. as the hour of observation. The want of this elimination becomes the more necessary the greater the deviation of the periodical oscillations, and still more requisite when this oscillation takes place in opposite directions at the stations to be compared. Now such is the case when we compare with each other places on the one and the

other side of the line of demarcation between the continental and the sea-climate. As these annual oscillations amount at Barnaul to $8\frac{1}{2}$ lines, it will be evident that considerable errors might be committed by not considering these relations in the levelling with the barometer. As journeys are generally undertaken during the summer months, it results that a much greater elevation above the Europæan stations will be ascribed to the Asiatic stations than they in reality possess*. The numerous anomalies which have been observed on the frontier of Europe and Asia between the barometrical and trigonometrical levellings, may receive more or less explanation from these relations. We were certainly not previously acquainted with such considerable and regular curves as those at Barnaul and Nertchinsk, except from the district of the monsoons, and were consequently not convinced of the necessity of a correction for the annual period. But the assumption, that the high land of Asia forms a boundary towards the north for this phænomenon of the periodical variation of the atmospheric pressure, is refuted by observations carried on for several years; we now know that it is exhibited with the same energy at the Altai as in the low land of the Ganges, and is far more considerable there than at the mouth of the Mississippi; and that the barometrical relations of Bombay are repeated at Nicolaieff; annual means only therefore can be employed for barometrical levellings of the plains.

What is represented in the drawings is expressed in the numerical values of the Tables at pp. 489 to 493. I have based their calculation on the most trustworthy and recent observations which have been accessible to me. All of them, with the exception of some localities in Table VI., are corrected for the thermal expansion. Table IX. leaves most to desire, because we do not yet possess the means for eliminating the daily oscillation resulting from the elasticity of the vapour. For the calculation of the averages, I have selected those hours which appeared to give the nearest approximation; I must not however enter into the details of the calculations. The number of hygrometrical observations being limited, it appeared to me most appropriate, in order to determine the pressure of the dry air, to combine the results for the elasticity of the vapour, for such as were extant, with the longest series of annual results for the barometer, even when hygrometrical observations did not exist for every

* See Galle in Poggendorff's *Annalen*, vol. xlviii. pp. 58, 379.

year in this series; since the monthly means of single years differ less hygrometrically than barometrically. This in fact justifies the course adopted. There being no barometrical observations for Lugan, the vapour curve of that place is combined with the barometrical for Taganrog. From the proximity of the places of observation, the error committed can be but inconsiderable. The exponent affixed to the names of the localities indicates the number of years from which the means have been calculated.

If we determine the differences of temperature of the coldest and warmest month in degrees of Reaumur, we find for Nertchinsk 38°·3, Barnaul 34°·3, Bogoslowsk 33°·1, Slatoust 35°·8, Catharinenburg 28°·2, Kasan 27°·3, Archangel 25°, Moscow 22°·9, St. Petersburg 21°·8, Wilna 18°·2, Cracow 19°·5, Prague 18°·0, Berlin 17°·5, Regensburg 17°·3, Stuttgard 17°·9, Carlsruhe 15°·8, Maestricht 15°·3, London 12°·5. The continually increasing bend of the curve for the pressure of the dry air in advancing from the west coasts of Europe into the interior of North Asia thus receives its explanation. But if we observe the numbers of Table IX. under the head oscillation, we find for the Asiatic stations nearly the same numbers as for the Europæan, by oscillation being understood the difference between the month with the highest and that with the lowest pressure of vapour. With the slight concave bend of the Europæan curves for the pressure of the dry air the convex bend of the curve of the vapour consequently preponderates; while for the Asiatic stations of observation the reverse happens. The complicated problem in Europe is solved in a very simple manner if we refer the pressure of the dry air, as well as that of the vapour, to a straight axis of the abscissa.

Von Humboldt first showed that near the equator the mean barometrical pressure on the surface of the sea is less than in the latitude of Paris, but Von Buch has called our attention to the high mean barometrical pressure near the Canary Islands. That between those two extremes a gradual transition occurs, that the pressure consequently continually decreases in approaching the zone of the trade-winds from the tropics to the region of calms, has been found by direct observations by A. Erman and Herschel, and is likewise confirmed by the ships' journals of Ryan and MacHardy, Quevedo, Beechey, Horner, Spencer and Lund. The phænomenon of the trade-winds however is not invariably fixed throughout the year to the same geographical latitude, but

it advances and recedes with the sun, though in a much smaller proportion. Each locality in the trade-zone approaches therefore in the year to the exterior and to the interior limits of the trade-winds, or barometrically speaking, to the region of high and diminished barometrical pressure. It must therefore exhibit within the annual period a periodical change of the atmospheric pressure. The greater this displacement, the greater the bend of the barometrical curve of the place. The greatest displacement obtains in the district of the monsoons; for here the south-east trade-wind, in the form of the south-west monsoon, follows the sun into the latitude of 30°. The barometrical oscillation will consequently be the greatest at this spot, as exhibited by the curves of Table III.

But whence this considerable advance?

From the western extremity of the Sahara to the eastern of the Gobi, in an extent of 132° of longitude, a wide, uninterrupted waste belt, as Von Humboldt observes, extends through the centre of Africa, Arabia, Persia, Candahar and the Mongoley. But there the sand by insulation acquires a temperature under the influence of a more or less vertical sun, which is found neither in the prairies of the Mississippi nor in the primitive forests of the Orinoco and Amazon river. With the increasing northern declination of the sun therefore we meet in Hindostan with temperatures such as are not known at any other place of the globe, Nagpoor, Benares, Mozufferpur, Nasirabad, Seharunpur, 25° to 29° R. in the middle of May and June. The power of the north-east monsoon is completely broken by this, and a vast ascending current is formed over the compact mass of land of Asia, which, on the one hand, draws the south-east trade-wind, in the form of a south-west monsoon, as far as the base of the Himalaya, and, on the other hand, may cause in Europe, during the summer, that constant western direction of the wind from the Atlantic, which does not participate in this rise of temperature, and which in the summer extends the character of the sea-climate further into the continent than would otherwise be the case. If we consider that in Iakutzk, over a soil which is during the whole year frozen to a depth of 400 English feet, the temperature of the air rises to above 16° Reaumur; that there, where the mean temperature of January falls below the freezing-point of mercury, this soil bears larch forests on its surface, that spring-wheat, rye, potatoes, cabbage and turnips are cultivated

in it, the assumption, that the region of calms has here temporally approached the Arctic region in a manner which does not occur in any other part of the globe, will no longer appear daring. Again, bearing in mind that Christiansborg, on the coast of Guinea, belongs to the southern hemisphere, in its barometrical relations, that according to Burnes (Cabool, App. 318) south winds prevail from May to September in the valley of the Indus, that in Chusan the northern monsoon only sets in in October, while during the summer months calms appear to predominate rather than a real south monsoon; when we see that the barometrical oscillation, decreasing in Seringapatam, Katmandu, Mussuree, Kotgurh, Simla, Darjiling, in the high land in Hindostan generally (*Repertorium*, iv. p. 236), again attains the same magnitude in the steppes of Barabinsk as in the low land of the Ganges; when the rainy season in southern Siberia occurs at the same period as on the southern declivity of the Himalaya, without being interrupted by winter rains, as is the case at the exterior limits of the trade-wind,—the whole of these phænomena are more simply explained by admitting the occurrence of an ascending current of air over south and central Asia during the summer. If this region of diminished atmospheric pressure forms a point of attraction for neighbouring masses of air, it appears with all the characters of the region of calms, which consequently rotates during the annual period about a more or less stationary point, situated in America, in such a manner that at its greatest elongation to the north in the summer it reaches into Asia, but in the winter recedes to the south, followed immediately by the north-east monsoon, which re-establishes the normal relations.

This change reacts very considerably on the relations of the weather in Europe. The axis of the thermal wind-rose, which in the winter connects the warmest point at south-west with the coldest at north-east, changes to such an extent, that in the summer, on the contrary, the coldest point falls in a western, the warmest in an eastern direction. While in the winter the barometrical extremes of the wind-rose coincide with its extremes of temperature, this no longer takes place in the summer; on this account the barometer is a far more certain guide for judging of the weather in the winter than in the summer. Moreover, the barometrical wind-roses of more easterly localities will necessarily be less regular than those of western places. It is

therefore evident that we must not attribute the annual periodical variation in the pressure of the atmosphere solely to the influence of the direction of the wind; and the figures in Table VIII., in which this influence is eliminated by calculation, actually show how inconsiderable this influence is, as I proved sixteen years ago (*Annalen*, vol. xi. p. 583). It would likewise be perfectly useless to attach any weight to the short apices of the Europæan barometrical curves, after the entire phænomenon has been ascertained to be a transition between the phænomena of sea-climate and those of continental climate; for that would be making the particular configuration of the coasts of Europe take part in this problem. It will be time for such local examinations when the general one is well-determined. The sudden bend of the North Asiatic curves (a concave bow between two more or less horizontal branches), in opposition to the uninterrupted curve of the localities in the district of the monsoons, will probably remain. We find North Asia suddenly drawn into a circle of phænomena to which it does not belong. It is a violent arousal from winter slumber, not a gradual and regular transition of relations mutually affecting each other, but the abrupt antitheses of the continental climate are without any intermediation.

We are accustomed to compare the continental character of the climate of North America without hesitation with that of North Asia. This view is in my opinion erroneous, even in respect to temperature. North America and the arctic countries, covered with large surfaces of water, differ from Asia in their relations of temperature precisely by their not having that high summer temperature. We look in vain for the July temperature of Iakutzk, 16° to 17° R. at the Slave lake; in Ustjansk it is 12°, in Boothia only 4°. The barometrical conditions in America are far more closely related to those of the sea-climate. If, for instance, we observe the form of the curve of Reikiavig in Iceland, where the pressure from February to May increases, and then almost uninterruptedly falls until December, differing altogether from the Europæan and Asiatic barometrical curves, and compare with that (Table VI.) the stations of observation of the polar expeditions, of which however the observations at Winter island, Melville island, and Igloolik still require a considerable correction, on account of the constant temperature of the ships, we also find a corresponding maximum in May. The rarefaction during the summer months is certainly well-marked, even in this

case; but it is very improbable that, if it exists at all in the temperate zone, it attains there the same extent as in Asia; at least no trace of it is found in the series of observations for six years at Ancaster, between the Ontario and Erie, but a gradual rising from June to September, while the five years' series at St. John's, in Newfoundland, approaches more to Iceland, and those at Cambridge in Massachusetts, which are corrected for temperature, represent the transition to Europæan relations.

2. *Daily Variations.*

With respect to the influence which the elasticity of the vapour mixed with the dry air exercises upon the extent and course of the daily oscillation, we likewise perceive, as in the annual variations, that it must differ considerably, according as the place of observation is situated near the sea or far from it. For a locality of the former description, I have shown by calculation of the observations of Appenrade (Poggendorff's *Annalen*, vol. xxii. p. 219), that in the annual average the daily curve of the elasticity of the vapour shows no bend at all, but rises uninterruptedly from the coldest hour of the day to the warmest, and then in like manner uninterruptedly decreases; and that if we calculate from this the changes of the pressure of the dry air, they lose the morning maximum, and follow a period of twenty-four, not of twelve hours, and are consequently very closely related to the curve of the daily variations of temperature. Since then the observations of Plymouth have confirmed this result. But in places distant from the sea, where no sea-wind during the day can restore the humidity carried away by the ascending current from the lower strata, the elasticity of the vapour will not be able to replace what the air loses by thermal rarefaction; we have therefore to expect that the morning maximum for the whole atmosphere will disappear, just as occurs at places near the sea, for the pressure of the air only when separated from the elasticity of the vapour. Now this really happened at Barnaul in the years 1838 and 1840 (the year 1839 only shows quite an irregular course), in Catherinenburg and Nertchinsk, in the mean of several years; lastly, at Slatoust the compensation appears perfect, while St. Petersburg and Bogoslowsk still exhibit a morning maximum. But if we eliminate the vapour, all the curves give the determinations found for Appenrade, as shown in the following tables (English inch):—

A. *Petersburg*[5].

	Barometer.	Elevation of the vapour.	Dry air.	Temp. R.
8	29″·9721	0″·2142	29″·7579	2°·278
10	·9762	0·2376	·7386	3·138
11	·9767	0·2560	·7207	3·822
2	·9725	0·2624	·7101	4·118
4	·9690	7·2526	·7174	3·694
6	·9673	0·2348	·7325	3·022
8	·9675	0·2148	·7527	2·244
10	·9679	0·1986	·7693	1·612
Osc.	0·0094	0·0638	0·0592	2·506

B. *Catherinenburg*[5].

	Barometer.	Elevation of the vapour.	Dry air.	Temp. R.
8	29″·0768	0″·1778	28″·8990	−0°·676
10	·0763	0·1856	·8907	1·056
12	·0716	0·1816	·8900	2·454
2	·0678	0·1798	·8880	2·876
4	·0663	0·1796	·8867	2·456
6	·0673	0·1816	·8857	1·308
8	·0712	0·1856	·8856	0·300
10	·0732	0·1854	·8878	−0·802
Osc.	0·0105	0·0060	0·0134	3·678

C. *Slatoust*[4].

	Barometer.	Elevation of the vapour.	Dry air.	Temp. R.
8	28″·7608	0″·1939	28″·5667	−1°·435
10	·7609	0·2024	·5585	0·530
12	·7554	0·2087	·5467	2·185
2	·7502	0·2123	·5379	3·018
4	·7492	0·2122	·5370	3·073
6	·7515	0·2087	·5428	1·998
8	·7551	0·2037	·5514	0·233
10	·7566	0·1917	·5649	−1·423
Osc.	0·0117	0·0206	0·0297	4·508

D. *Bogoslowsk*[2].

	Barometer.	Elevation of the vapour.	Dry air.	Temp. R.
8	29″·2143	0″·162	29″·052	−2°·070
10	·2163	0·185	·031	−0·535
12	·2153	0·206	·009	0·645
2	·2113	0·215	28·996	1·245
4	·2085	0·212	·996	0·995
6	·2103	0·197	29·013	0·135
8	·2113	0·183	·028	−0·950
10	·2150	0·166	·049	−2·195
Osc.	0·0078	0·053	0·056	3·440

D. *Nertchinsk.*

	Barometer.	Elevation of the vapour.	Dry air.	Temp. R.
8	27″·7120	0″·151	27″·5610	−5°·030
10	·7105	0·172	·5385	−3·160
12	·7080	0·193	·5150	−1·640
2	·7045	0·209	·4955	−0·615
4	·7038	0·213	·4908	−0·680
6	·7040	0·202	·5020	−1·365
8	·7063	0·185	·5213	−1·470
10	·7093	0·176	·5333	−3·595
Osc.	0·0082	0·162	0·0702	−4·415

On the whole, we perceive a perfect parallelism between the annual and daily periodical variations, a surprising simplification of a most complicated phænomenon, as soon as we separate the pressure of the dry air from the elasticity of the vapours. But in like manner, as the periodically varying direction of the wind exercises an influence, however small, upon the annual oscillations, there may exist co-operating causes for the daily changes, which have not been taken into account in the present investigation*. But whatever explanation we may give of these causes, the fact of that simplification is established and confirmed by observations extending from England to Nertchinsk, and no theory of these phænomena can disregard it. It is an essential part of the phænomenon itself.

To enter into a similar examination for the tropical regions would be most important for the explanation of the phænomenon. From the constant direction of the trade-wind, a separation of the dry air and the vapour-atmosphere appears less requisite there; but this can only be decided when we can compare a place of the continental climate to one of the sea-climate within the tropics also. This however will probably long remain a vain wish.

* I have entered more largely into some of them in a former treatise (*Annalen*, vol. xxii. p. 219). As hourly observations are now making at several Russian stations, a more strict investigation of the present problem will be possible at a future period.

Pressure of the Atmosphere 300''' + (Par.)

	Jan.	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Oscill.
I.—Sea-climate.													
Palermo[20]	34·69	34·96	34·17	33·99	34·46	34·89	34·59	34·81	34·95	34·68	34·84	35·02	
Milan[20]	33·44	33·46	32·67	31·94	32·68	32·93	33·06	33·15	33·28	35·75	33·35	33·61	
Strasburg[15]	33·13	33·45	32·91	32·45	32·52	33·41	33·17	33·35	33·63	32·98	32·87	32·70	
Carlsruhe[33]	34·55	34·61	33·96	33·30	33·56	34·08	34·10	34·14	34·18	34·18	33·88	34·20	
Stuttgard[15]	29·35	29·06	28·33	28·00	28·19	28·82	28·95	28·74	29·68	28·42	28·21	28·95	
Munich[12]	17·71	17·66	16·66	16·41	16·95	17·59	17·95	17·56	17·70	17·93	17·15	17·32	
Regensburg[54]	24·27	24·18	23·69	23·35	23·78	24·14	24·24	24·44	24·60	24·43	24·03	23·64	
Hof[8]	19·22	18·59	18·35	18·24	18·87	19·32	19·48	19·16	19·06	19·36	18·16	19·27	
Prague[10]	30·25	30·47	28·92	28·97	29·75	29·41	29·44	29·67	30·16	29·67	29·66	29·49	
Zittau[12]	28·27	27·97	27·24	26·70	27·60	27·73	27·82	27·62	27·94	28·87	27·78	28·31	
Freiberg[9]	22·47	22·05	21·49	20·82	22·06	21·99	22·31	21·91	21·96	22·76	21·61	21·84	
Dresden[10]	33·87	33·47	32·68	31·92	32·95	32·91	32·92	32·72	33·07	34·07	33·27	33·56	
Halle	34·53	34·00	33·19	32·90	33·61	33·67	33·92	33·44	33·99	34·93	33·92	34·29	
Berlin[4]	36·22	36·45	35·11	34·94	35·61	35·81	35·50	35·82	35·87	35·94	35·47	35·39	
(St. Bernhard[10]) 200 +	48·30	46·68	48·14	48·89	49·54	50·26	51·53	51·79	51·16	49·74	49·04	48·68	
II.—Transition of the Sea-climate into Continental.													
Breslau[8]	32·29	32·36	31·71	31·26	31·57	31·96	32·02	32·09	32·15	31·68	31·35	33·19	
Ofen[4]	29·34	28·94	28·24	27·41	27·53	28·62	28·51	28·75	28·97	29·62	27·83	29·94	
Cracow[11]	30·19	30·02	28·85	28·44	28·95	29·18	29·16	28·86	29·64	30·18	29·46	29·38	
Wilna[5]	33·01	33·41	32·71	33·11	33·26	33·63	33·06	33·10	34·28	33·91	33·26	31·66	
St. Petersburg[13]	37·08	38·28	37·24	37·43	37·32	36·83	36·13	36·61	37·43	37·27	36·44	36·91	
... ... [5]	36·56	37·59	37·36	38·70	37·76	36·07	36·27	36·29	38·12	38·19	37·27	37·88	

	Jan.	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Oscill.
III.—Continental.													
Nicolaief[7]	38·09	37·54	36·95	35·87	35·61	35·43	35·13	35·77	36·86	37·05	37·03	37·83	2·96
Taganrog[1]	38·87	37·58	37·77	36·20	36·61	35·46	35·80	36·50	37·20	39·51	39·51	40·61	5·15
Moscow[4]	30·11	30·10	29·84	29·80	29·02	27·30	28·97	29·19	31·53	30·85	30·25	32·79	5·49
Kasan[10]	35·46	36·86	35·72	35·39	33·88	32·98	32·34	33·06	34·44	35·75	34·46	35·25	4·52
Slatoust[4]	24·83	24·71	24·38	24·18	23·14	21·65	21·87	22·75	23·49	25·04	24·97	24·08	3·39
Bogoslowsk[2]$\frac{1}{2}$	29·36	30·74	30·32	28·51	29·14	27·45	28·38	28·61	28·90	31·22	29·55	31·02	3·77
Catharinenburg[5]	28·40	28·43	27·95	28·51	26·46	25·15	25·14	26·17	26·82	28·51	28·55	27·84	3·41
Barnaul[3]	37·39	35·95	35·31	33·64	31·56	29·16	28·89	30·01	30·85	35·35	34·64	35·72	8·50
Nertchinsk[2]	14·91	13·86	12·77	11·43	10·14	10·29	9·59	10·97	11·54	12·00	12·76	13·36	5·32
IV.—(District of the Monsoons.)													
Chusan	42·42	42·58	.....	.....	.....	.....	.....	.....	38·09	39·77	39·94	41·66	
Macao[1]	40·41	40·01	39·60	37·76	37·63	35·71	35·98	35·98	37·89	38·40	39·64	40·74	4·70
Canton[10]	39·76	38·90	37·99	36·09	35·09	34·75	33·91	33·94	34·23	36·78	38·59	39·17	5·85
Calcutta[8]	38·93	36·92	35·12	33·99	32·99	31·71	31·14	31·97	33·38	34·63	36·11	37·77	7·79
Benares[2]	34·87	33·76	33·00	31·29	30·26	28·54	28·33	29·51	30·69	32·63	33·83	34·90	6·54
Mozufferpur[3]	34·29	33·61	32·32	31·40	29·74	29·17	28·84	29·40	30·25	32·13	34·13	34·22	5·45
Madras[21]	37·34	37·18	36·70	35·67	34·37	34·44	34·59	34·75	35·10	35·54	35·79	37·11	2·97
Seringapatam[1]	11·01	10·45	9·56	8·65	8·34	8·11	8·29	8·30	8·52	9·31	9·55	9·69	2·90
Poonah[3]	16·25	15·29	14·73	14·23	12·56	12·45	12·87	13·49	14·35	14·69	15·76	16·03	3·60
Bombay[1]	37·97	37·66	37·16	36·20	35·68	35·07	34·17	34·41	35·34	36·71	37·12	37·26	2·90
Nasirabad[4]	20·61	19·62	18·83	17·79	16·49	15·23	14·97	15·54	16·81	18·70	20·12	20·34	5·64
V.—(Extreme limits of the Trade Winds.)													
Funchal[3]	38·44	37·71	37·66	37·03	38·07	38·21	37·91	37·97	37·84	38·03	37·58	39·03	
Natchez[5]	35·66	34·53	33·98	33·64	33·37	33·23	33·64	33·51	33·79	34·57	35·53	35·14	

	Jan.	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Oscill.
VI.—Polar countries*.													
Port Bowen[1]	35·49	36·50	38·99	38·54	38·36	36·52	35·72	34·21	34·28	37·36	36·64	36·31	3·77
Boothia Felix[2]	35·79	37·50	37·36	37·71	39·37	38·04	36·55	36·18	35·82	37·30	37·17	36·87	3·58
Melville Island	.....	.....	35·56	37·54	39·01	35·79	34·05	34·70					
Winter Island	.....	.....	34·27	34·81	35·90	34·60	32·56	32·16					
Igloolik	.....	.....	38·11	37·44	36·82	37·01	32·56	35·01					
Reikiavig[14]	31·78	29·98	31·58	33·99	34·68	34·60	34·26	33·96	32·31	31·67	31·96	29·61	2·90
Eyafiord[2]	31·4	29·3	33·3	36·7	37·2	34·6	35·0	34·4	32·9	31·8	33·5	35·5	5·8
Greenland Ocean, 70° B.	.....	.....	.....	35·10	36·93	36·23	36·05						
Kaafiord[2], near Alten†	31·87	35·14	32·79	33·81	33·84	34·26	32·21	33·83	34·87	36·42	34·03	34·29	1·95
VII.—(Coasts of the Atlantic.)													
Cambridge, N. A.	37·70	37·66	37·78	37·58	37·52	37·57	37·77	38·02	38·51	38·34	37·54	37·01	
London[20]	36·42	36·03	36·21	35·94	86·53	36·39	36·48	36·36	35·79	36·54	35·35	36·41	
Paris[26]	35·68	35·56	35·12	34·46	34·67	35·34	35·27	35·17	34·95	35·03	34·75	35·30	
Maestricht[16]	36·57	36·18	35·40	34·84	35·55	35·89	35·87	35·60	35·68	35·66	35·48	35·45	
VIII.—(Influence of the direction of the Wind eliminated.)													
Reikiavig	37·43	35·47	36·86	38·43	34·24	34·14	33·81	32·67	32·07	31·30	31·25	30·34	
St. Petersburg	37·73	38·15	36·98	37·28	37·00	36·66	35·96	36·51	37·19	37·30	36·28	37·03	
Carlsruhe	34·07	34·18	33·67	33·07	33·43	33·90	33·80	34·01	34·15	34·02	33·66	33·53	

* By oscillation is here understood the difference between January and May.
† Ihle's Observations, communicated in MSS. by Professor Reich.

IX.—*Elasticity of the Aqueous Vapour.* (Paris lines.)

	Jan.	Feb.	March.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Oscill.
London[15]	2·42	2·59	2·89	3·31	4·06	4·76	5·43	5·46	4·85	4·01	3·18	2·84	3·04
Brussels[2]	2·24	2·15	2·63	3·19	4·32	4·44	4·81	4·92	4·92	3·72	2·97	2·70	2·77
Breda[2]	1·88	2·23	2·47	2·62	3·46	4·89	5·06	4·71	4·67	3·86	2·29	2·57	3·18
Milan[1]	2·19	2·29	2·08	3·32	4·46	5·58	5·42	6·22	4·73	3·59	3·28	2·17	4·14
Carlsruhe[6]	1·78	1·94	2·13	2·44	3·48	4·74	4·84	5·12	4·38	3·44	2·58	1·97	3·34
Stuttgard[6]	1·77	2·00	2·17	2·27	3·40	4·37	4·67	4·77	4·08	3·23	2·49	2·05	3·00
Munich	.....	.....	.....	2·67	3·89	4·05	4·32	4·54	4·37	3·34	2·23	2·11	
Hof[3]	1·39	1·50	1·65	1·97	3·07	4·06	4·20	4·29	3·78	2·80	2·25	1·78	2·90
Prague[2]	1·39	1·55	1·98	2·97	3·98	4·57	4·99	4·70	4·43	3·31	2·94	1·67	3·60
Jena[3]	1·96	2·11	2·72	2·45	3·70	4·13	4·91	4·42	4·09	2·95	2·28	2·18	2·95
Halle	2·00	2·11	2·26	2·77	3·47	4·54	5·15	4·74	4·24	3·49	2·50	2·48	3·15
Appenrode[4]	2·34	2·24	2·57	3·50	4·28	5·44	6·13	5·97	5·53	4·34	2·90	2·79	3·89
Breslau	1·66	1·69	2·13	2·70	3·85	4·67	4·93	4·96	4·34	3·32	2·40	1·78	3·30
Cracow[5]	1·16	1·46	1·57	2·23	2·90	3·69	4·25	4·19	3·55	2·78	1·75	1·50	3·09
St. Petersburg[5]	1·23	1·23	1·41	1·95	2·74	3·54	4·59	4·67	3·80	2·51	2·04	1·20	3·47
Lugan[3]	1·19	1·26	1·56	2·08	3·38	4·79	5·07	4·35	3·10	2·56	1·21	1·36	3·88
Kasan[1]	0·68	1·02	1·52	2·29	2·49	3·41	4·34	4·12	2·95	2·27	1·13	0·37	3·75
Slatoust	0·77	0·53	1·00	1·96	2·95	4·72	4·35	4·37	3·05	1·72	1·22	0·83	4·19
Bogoslowsk[2]	0·70	0·54	0·91	1·88	3·25	4·18	4·97	4·10	2·62	1·71	0·88	0·42	4·55
Catherinenburg[5]	0·80	0·77	1·05	1·39	1·94	3·72	4·40	3·98	2·72	1·80	1·17	0·70	3·70
Barnaul	.....	.....	.....	1·94	3·37	4·66	5·27	4·92	2·79				
Nertchinsk[2]	0·09	0·14	0·56	1·61	3·13	4·64	4·52	5·16	2·78	0·99	0·34	0·25	5·43
Chusan	3·26	3·03	.....	.....	.....	.....	.....	.....	11·03	8·67	4·95	2·93	
Calcutta[2]	4·53	5·88	7·25	8·35	10·59	10·69	10·64	10·74	10·15	9·38	6·45	5·62	6·22
Benares[3]	4·64	4·69	4·94	5·37	6·91	0·69	11·69	11·66	10·66	8·99	6·19	4·42	7·27
Nasirabad[4]	2·22	2·48	2·48	2·70	2·97	6·58	8·57	8·52	7·24	3·77	3·23	2·78	6·35
Seringapatam[1]	5·18	5·92	6·11	7·63	7·63	7·40	7·16	6·69	6·69	7·16	6·62	5·85	2·45
Poonah[3]	4·72	3·85	3·91	5·66	7·08	8·61	8·76	8·41	7·98	6·90	5·46	3·63	4·99

Pressure of the Dry Air 300^{m} + (Par.)

	Jan.	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Oscill.
London	34·00	33·44	33·32	32·63	32·47	31·63	31·05	30·89	30·94	32·52	32·18	33·57	3·11
Brussels	33·40	32·69	32·70	31·86	31·02	30·88	30·56	29·37	29·57	31·19	30·95	33·04	4·03
Milan	34·25	31·17	30·59	28·62	28·22	27·34	27·64	26·94	28·55	30·16	30·07	31·45	4·11
Carlsruhe	32·77	32·69	31·83	30·86	30·08	29·34	29·26	29·02	29·80	30·74	31·30	32·23	3·75
Stuttgard	27·59	27·06	26·16	25·73	24·79	24·45	24·28	23·97	25·60	25·19	25·72	26·90	3·61
Hof	17·73	17·09	16·70	16·27	15·80	15·26	15·28	14·85	15·28	16·56	15·91	17·49	2·98
Prague	28·86	28·92	26·94	26·00	25·77	24·84	24·45	24·97	25·73	26·36	26·72	27·82	4·47
Halle	32·68	31·98	30·91	30·20	30·09	29·14	28·81	28·68	29·59	31·54	31·39	31·85	4·00
Appenrode?	35·23	34·27	33·76	33·01	32·16	31·00	30·41	30·47	31·33	31·73	32·37	32·48	4·82
Breslau	30·63	30·67	29·58	28·56	27·72	27·29	27·09	27·13	27·81	28·36	28·95	31·41	4·32
Cracow	29·03	28·55	27·27	26·21	26·05	25·49	24·91	24·67	26·09	27·40	27·89	27·96	4·36
St. Petersburg	35·33	36·37	35·95	36·75	35·03	32·53	31·67	31·62	34·32	35·69	35·23	36·67	5·13
Taganrog	37·67	36·32	36·21	34·12	33·23	30·67	30·74	32·15	34·10	36·99	38·30	39·25	8·51
Kasan	34·78	35·84	34·20	33·19	31·39	29·57	28·00	28·94	31·49	33·48	33·33	34·88	7·84
Slatoust	24·06	24·18	23·37	22·23	20·19	16·93	17·53	18·38	20·44	23·32	23·75	23·24	7·25
Bogoslowsk	28·67	30·20	29·41	26·63	25·88	23·27	23·42	24·50	26·28	30·51	28·66	30·60	6·33
Catherinenburg	37·60	37·66	36·90	37·11	34·52	31·43	30·74	32·19	34·09	36·71	37·38	37·14	6·92
Barnaul *	37·30	35·82	34·75	31·71	28·19	25·03	23·62	25·08	28·06	34·36	34·31	35·47	13·68
Nertchinsk	14·82	13·72	12·21	9·82	7·01	5·65	4·08	5·81	8·76	11·01	11·42	13·12	10·74
Chusan	39·16	39·55	.....	.....	.....	.....	.....	.....	27·06	31·10	34·99	38·73	12·1
Calcutta	32·80	31·12	28·69	26·93	22·15	21·52	21·32	21·78	23·57	25·93	31·06	32·01	11·48
Benares	30·19	29·20	28·11	26·08	23·35	17·92	16·35	17·94	20·16	23·56	27·73	30·36	14·01
Nasirabad	18·39	17·14	16·35	15·09	13·52	8·65	6·40	7·02	9·57	14·93	16·89	17·56	11·99
Seringapatam	5·83	4·83	3·45	1·02	0·71	0·71	1·13	1·61	1·83	2·15	2·93	3·84	5·12
Poonah	11·53	11·44	10·83	8·56	5·48	3·84	4·11	5·01	6·36	8·78	10·30	12·40	8·56

* The six months of the elasticity of the vapour wanting under Barnaul are placed after Nertchinsk.

Article XVII.

Remarks on the Polarization of Light by Reflexion, especially by doubly refracting bodies, with an abstract of Mr. MacCullagh's *Treatise on the same subject. By* A. Seebeck.

[From Poggendorff's *Annalen*, vol. xxxviii. No. 6, 1836.]

As is well known, Fresnel by his theory of double refraction was led to the view that in polarized light the vibrations of the æther take place at right angles or perpendicular to the plane of polarization. With this idea he and others developed formulæ for the intensity of the reflected light*. In so doing he added the two following premises:—1st, that in the two media, on the surfaces of which the reflection and refraction occur, the æther has *the same elasticity*, but a *different density*; 2nd, the dislocations of the particles of æther parallel to the surface of separation are equal in both media. On these suppositions (preserving the former signs), the amplitude of a ray which before reflexion was polarized parallel to the plane of polarization was $-\frac{\sin(i-i')}{\sin(i+i')}$, that of one polarized in a perpendicular plane was $-\frac{\tan(i-i')}{\tan(i+i')}$; these formulæ were confirmed by observation. But since it has been shown by Cauchy and Neumann, from the more strict theories of double refraction, that the vibrations must be considered as *parallel* to the plane of polarization, the above formulæ must be inverted, the second applying to the first and the first to the second case, whence they are no longer in accordance with experience. This difficulty however is removed by admitting that the æther possesses the *same density* in both media, but *different elasticity* instead of the supposition expressed in 1, and preserving the auxiliary hypothesis 2. For as the masses of æther in motion in the two media are now in the relation of $\sin i \cos i : \sin i' \cos i'$, according to the law of active forces, we have

$$\sin i \cos i\,(1-v^2) = \sin i' \cos i' \,.\, u^2.$$

* *Ann. de Chimie et de Phys.* tome xlvi.

Consequently the auxiliary hypothesis 2 for a ray polarized in a plane parallel to that of incidence, is

$$(1 + v) \cos i = u \cos i',$$

for one polarized at right angles,

$$1 + v = u;$$

hence for the former $v = \dfrac{\sin (i - i')}{\sin (i + i')}$,

for the latter $v = \dfrac{\tan (i - i')}{\tan (i + i')}$,

consequently the same formulæ as above, but with reversed signs*.

A similar alteration must be made in the calculation which I made on calcareous spar, whereby the formula there given may be carried out with somewhat more strict limits, whilst the inconvenience resulting from the supposition of a uniform elasticity of the æther vanishes. For if we assume the density in both media to be equal, $\cos \alpha : \mathrm{P} \cos \eta$ (the same signs being used as before) is the proportion of the magnitude of the wave of a ray incident in the plane of the principal section, to that of the extraordinary ray; hence, when the incident light is polarized in a plane perpendicular to that of incidence, according to the law of active forces,

$$\cos \alpha \, (1 - v^2) = \mathrm{P} \cos \eta \, . \, u^2,$$

and according to the auxiliary hypothesis 2,

$$1 + v = u.$$

Thus $v = \dfrac{\cos \alpha - \mathrm{P} \cos \eta}{\cos \alpha + \mathrm{P} \cos \eta}$;

this is likewise the original formula with opposite signs. Hence, as before,

$$\cos \alpha = \mathrm{P} \cos \eta$$

is the equation, which gives the angle of polarization α when the plane of reflexion is parallel to the principal section.

Mr. MacCullagh† has treated this subject and rendered the formulæ more universally applicable. The premises with which

* Be the sign what it may, the formulæ in each case show that in external reflexion it is opposite to that in internal, as Young supposed in explaining the phænomenon that Newton's coloured rings in refracted light are complementary to those in reflected light, a phænomenon which is otherwise explained in a much more artificial method, by the so-called loss of half a wave. Vide Herschel, 'Light,' § 674.

† London and Edinburgh Philosophical Magazine, Feb. 1836.

he starts are these:—1st, he supposes that the vibrations are parallel to the plane of polarization, but modifies Cauchy's equations so that the known third system of waves is dispensed with, thus the refraction at once accurately comes to the same as in Fresnel's theory; 2nd, the resultant of the incident and reflected vibrations in reference to their direction and length is equal to that of the refracted; 3rd, the perpendicular pressure on the plane of incidence is equal to that on the surface of separation in both media. Now if we suppose a sphere to be described at the point of incidence, and that I Z be the weight of incidence, I P the axis of the crystal, the great circle Z O E the plane of incidence, I O the ordinary ray produced backwards, and I E the normal of the extraordinary wave, let $ZO=\varphi$, $ZE=\varphi'$, $PO=\psi$, $PE=\psi'$, $<ZOP=\Theta$, $<ZEP=\Theta'$; let i' be the angle of incidence, b and a the reciprocals of the ordinary and extraordinary index of refraction. Each of the two refracted rays may be made to disappear by polarizing the incident ray in a certain direction. When the extraordinary ray disappears, the plane of polarization of the reflected light forms with the plane of incidence the angle β, in which

$$\tan\beta=\cos(i+\phi)\tan\Theta+2(a^2-b^2)\sin\Theta\sin\psi\cos\psi\frac{\sin^2 i}{\sin(i-\phi)}. \quad (2.)$$

When the ordinary ray disappears, the plane of polarization of the reflected light with the plane of incidence forms the angle β', for which

$$\left.\begin{aligned}-\tan\beta' &= \cos(i+\phi')\cot\Theta' \\ &+(a^2-b^2)\frac{\cos 2\Theta'}{\sin\Theta'}\sin\psi'\cos\psi'\frac{\sin^2 i}{\sin(i-\phi')}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3.)$$

When β and β' become equal, the plane of polarization of the reflected ray becomes independent of that of the incident, and the angle of incidence, at which this occurs, is the angle of polarization. Hence

$$\left.\begin{aligned}&\cos(i+\phi)\,tg\,\Theta+2(a^2-b^2)\sin\Theta\sin\psi\cos\psi\frac{\sin^2 i}{\sin(i-\phi)} \\ &+\cos(i+\phi')\cot\Theta' \\ &+(a^2-b^2)\frac{\cos 2\Theta'}{\sin\Theta'}\sin\psi'\cos\psi'\frac{\sin^2 i}{\sin(i-\phi')}\end{aligned}\right\}=0 \quad (4.)$$

is the general conditional equation for the angle of polarization. Since $i+\phi$ is very nearly a right angle, if we make $i+\phi=90^\circ+\delta$, δ will be a very small magnitude. If we now make P R perpen-

dicular to Z O E and Z R = p, P R = q, we obtain more nearly and without reference to the reflexion in passing from air into calcareous spar*,

$$\delta = \mathrm{K}\cos^2 q\,(\cos^2\phi - \cos^2 p), \text{ in which } \mathrm{K} = \frac{(a^2-b^2)(1+b^2)}{2\,b(1-b^2)} \quad (5.)$$

When the axis lies in the plane of incidence, from the equation (4.) we can deduce

$$\sin^2 i = \frac{1 - a^2\sin^2\lambda - b^2\cos^2\lambda}{1 - a^2 b^2},\ \lambda \text{ being} = \mathrm{Z\,P}.$$

The latter equation is that at which I arrived by my calculation, and which agrees very well with my observations. The angles of polarization calculated for other azimuths of the plane of incidence agree accurately with my measurements†, whilst the differences on the natural surface of fracture do not amount to more than three minutes, and in the case of the upper surfaces are not greater than might be expected considering the difficulty previously mentioned, that of procuring polished surfaces of calcareous spar with a perfectly uninjured condition of the surface. Brewster's measurements, to which Mr. MacCullagh refers for the confirmation of his theory, agree for the natural surfaces to within about one-fourth of a degree of those obtained by calculation, the difference amounts to three-fourths of a degree for a surface inclined 5° towards the axis.

Although Mr. MacCullagh's calculations agree well with my measurements in regard to the angle of polarization of calcareous spar, the same does not hold good in the case of the value of β and β'. I have previously mentioned, that, when a ray is polarized by the reflexion produced at the surface between the air and the calcareous spar, the plane of polarization does not in general correspond with that of incidence, but forms an angle with it. This angle must be that which Mr. MacCullagh expresses by β and β'; but the values calculated according to the equations (2.) and (3.) do not agree with the measurements which I made, but, for instance, for a surface parallel to the axis, in which each angle, according to observation, may amount to 4°, β and β' constantly or nearly so, are = 0, and do not differ less from experiment in the case of the natural surface of fracture. I shall take

* Mr. MacCullagh distinctly alludes to the rhomboids of calcareous spar only; however, what follows, shows that the equation (5.) agrees with observation in the case of other surfaces of calcareous spar.

† Poggendorff's *Annalen*, vol. xcvii. p. 309.

this opportunity of communicating the measurements I have spoken of, which were made several years ago, and with the greatest possible care. Thus, I found the following values of this angle with the natural surface of fracture of the crystal, and one polished parallel to its axis, in different azimuths of the plane of incidence.

Azimuth, π.	On the natural surface.	On that parallel with the axis.
° ′	° ′	° ′
0 0	0 0	0 0
22 30	+0 11	+2 43
45	+0 23	+3 57
67 30	−0 48	+2 46
90	−2 30	0 0
112 30	−3 34	
135	−3 38	
157 30	−2 9	
180	0 0	

I have marked the examined angle with + when the plane of polarization was turned towards the same side as the principal section, when reversed with −. By the azimuth 0 and 180° that condition is understood in which the principal section is parallel with the plane of incidence, and in a natural surface 0, when the truncated extremity of the crystal is applied to the eye, 180° when it is turned towards the incident light. This difference vanishes in the case of the surface parallel to the prism, whilst from 90° to 180° the same recurs, but in reversed order.

The results which are here detailed are averages of at least twenty observations, and those made upon the natural surface of fracture are possibly accurate to within a few minutes; this may be less frequent with the others, on account of the imperfection of the polished surfaces; still these do not differ materially from the true values.

SCIENTIFIC MEMOIRS.

VOL. IV.—PART XVI.

ARTICLE XVIII.

On the Structure and Characters of the Ganoidei, and on the natural Classification of Fish. By J. MÜLLER, *Professor of Anatomy in the University of Berlin* *.

[Read before the Academy of Sciences at Berlin, Dec. 12, 1844.]

NO branch of natural history presents a more striking proof of the importance of a knowledge of extinct fossil genera in the natural classification of animals generally, and in particular of living species, than ichthyology. Palæontology has essentially altered the basis of this part of the system. The great difference existing between the fossil remains of fish has required the formation of whole orders and families, which have few or no representatives in the present world; and the isolated forms which have lasted until our own times must vacate the position systematically assigned to them, to be included among the prevailing groups of a former world in perfectly distinct places, and in other orders. The propriety of these arrangements principally depends upon the correctness of the supposition, that the fundamental differences existing in the remains of skeleton and cuticular appendages which have come down to us, were connected with equally important and decided differences in the general organization. How far such connexion extends, however, can only be ascertained from an examination of the existing creation. Although the systematic results of the examination of fossil fish have become so extensive and important, nevertheless it is undeniable, that the anatomy of living fish has not been sufficiently determined and studied to

* Translated from the German by J. W. Griffith, M.D.

give stability to the attempts to arrange fossil and living fish in one system.

The cuticular appendages exhibit most remarkable and most readily ascertained differences between fossil fish. M. Agassiz applied them as the groundwork of his classification of fish generally, and formed his sections of the Cycloidei, Ctenoidei, Ganoidei and Placoidei, from them. The scales of living osseous fishes are usually imbricate, more or less rounded, and differ, excepting the bony shields, in their minute structure from true bones; they do not generally contain the radiating corpuscles of bones; their surface usually exhibits concentric, elevated lines, which are sometimes irregular.

The difference between the scales which have an undivided margin, or the Cycloid, and the ciliated or Ctenoid, is slight, and its systematic application is confined within narrow limits*.

The scales of the Ganoidei (Ag.) are entirely different. They are bony, generally of a rhombic form or quadrangular, seldom rounded or imbricate, their surface is always smooth and coated with a layer of enamel; they are generally arranged in oblique rows, those in each row being usually united to one another by a prolongation of the hinge. This remarkable kind of scales occurs in the existing creation in two genera of fish only, which were arranged by Cuvier in his *Clupeæ*, viz. in the genus *Lepisosteus* from the Mississippi, and *Polypterus* from Senegal and the Nile.

Cuvier was the first who perceived the identity of the scales of *Palæoniscus* from the Zechstein with the scales of *Lepisosteus* and *Polypterus*, and who directed attention to the similarity of the long upper tail-piece in *Palæoniscus* and the Sturgeons to the marginal covering of this plate with triangular *fulcra* (or ridge-tiles), and to the covering of the anterior margin of the back fin with similar laminæ in *Palæoniscus* and *Lepisosteus*. From this resemblance he concludes that the *Palæoniscus* should be arranged *either* near the Sturgeons *or* in the vicinity of *Lepisosteus*†.

The idea of giving up this alternative and combining these two categories, does not receive any notice in Cuvier's writings. In his examination of the fish belonging to the genus *Dipterus*, he says distinctly, that they agree with the fish found in the

* See my Treatise on the Natural Families of Fish, Wiegmann's *Archiv*, 1843.
† *Oss. Foss.* Nouv. ed. t. v. 2. 1824, pp. 307, 308.

copper slate, in the structure of the tail-fin, and in the insertion of all the rays into its inferior surface; that among such as are now in existence, *Lepisosteus* alone, and in a less degree the Sturgeon, possess this character; that he should rather arrange the fossils with the *Lepisosteus*, and that they belong with the latter to the abdominal Malacopterygians*.

Valenciennes and Pentland likewise state that *Dipterus* and *Osteolepis* should form new genera in the order of the Abdominal Malacopterygians.

Agassiz deserves the greatest praise for having discovered the identity in the structure of the scales of *Lepisosteus* and *Polypterus* with those of all osseous fishes of the old formation down to the Chalk, for having separated the Ganoidei as a distinct order, and for having discovered and distinctly separated their numerous genera, and ascertained their species. He said truly†, "L'établissement de l'ordre des Ganoides est à mes yeux le progrès le plus important que j'ai fait faire à l'ichthyologie." Equally important is the deduction from these investigations, that the types, according to which the vast majority of fish at present in existence are formed, first commence with the Chalk.

The Ganoid scales, as remarked by Agassiz, are in general imbedded in depressions in the skin exactly like the ordinary scales. The outer portion of the membrane of the depression is extremely delicate and adherent, and may even appear to be wanting, as in *Polypterus*; but in *Lepisosteus* the enamel of the scale is seen to be covered by an extremely fine membrane, in which a slight silvery lustre and even pigment is discoverable, and which is readily removable by friction.

In the structure of the skeleton, the Ganoidei again differ very materially from one another, for many have a skeleton which is completely bony, such as we find in the living *Lepisosteus* and *Polypterus*; while in other fossils the spinal column has remained partly in the fœtal condition, of a soft *chorda dorsalis*, with bony apophyses in rows, just as among the Sturgeons in living fish. They also exhibit the greatest variations in the form of the body, just as the two living genera are completely different from one another.

In many genera the vertebral column extends to the extremity of the upper tail-piece, as we find among living fish, in the

* Geol. Trans. 2nd Series, vol. iii. p. 125.
† *Poiss. Foss.* vol. ii.

Sturgeons, and in the Sharks. M. Agassiz designates these as *Heterocerci*. In many Ganoids, the extremity of the vertebral column extends only as far as the commencement of the upper tail-piece, it then has superior fin-rays, as in many living osseous fishes of the Salmon tribe, *Clupea*, &c. In other Ganoids the vertebral column divides the caudal fin into two equal segments, as in most of the osseous fishes; these are the *Homocerci*.

In a large number of Ganoid genera the fins are remarkable, from their anterior margin or first ray being furnished with prickly scales, *fulcra*; others have no traces of them. This difference is also marked in the living genera; for *Lepisosteus* possesses this structure, *Polypterus* does not. The fulcra principally cover that part of the anterior margin of the fin which lies free; but where the rays increase in length and appear behind one another at the anterior margin, the fulcra pass over their extremities from the shorter to the longer rays. In general, the Ganoids are related to the Abdominal Malacopterygians in the structure of the fins and in the position of the abdominal fins.

The characters of the orders have been taken by Agassiz from the scales, which are mostly angular, rhomboidal, or polygonal, and covered with enamel. He enumerates in his large work, *Recherches sur les Poissons Fossiles*, the families *Lepidoidei*, Ag.; *Sauroidei*, Ag.; *Pycnodontes*, Ag.; *Cœlacanthi*, Ag.; *Sclerodermi*, Cuv.; *Gymnodontes*, Cuv.; *Lophobranchii*, Cuv.; and remarks, that after these families, in the order of Ganoids, some orders of living fishes must be arranged, as the *Goniodontes*, *Siluroidei* and *Acipenseridæ*. Agassiz has recently added the *Lepidosiren* to the Ganoids.

We cannot expect, when we consider the slight assistance fossils render us, that the families should be separated by such marked distinctions as in living animals. The differences between the *Lepidoidei* and *Sauroidei* are really very slight. Thus the former have either sickle-shaped teeth in many rows, or they are blunt; the Sauroidei, in which *Lepisosteus* and *Polypterus* are included, have conical pointed teeth, among which smaller teeth sometimes occur. The difference in the form also, which in the Sauroids is somewhat more elongated, is, after all, not material, as we see in the natural families at present in existence, such as the *Characini* and *Scomberoidei*. Although the separation of these two families is merely artificial, still, as it

facilitates their distinction, it may be advantageously used. On the other hand, an artificial distinction becomes doubtful to us, if we deduce from it details of the age and development of families, as, for instance, that no fish belonging to the family of the *Lepidoidei* could last until the present period. The *Lepidoidei* are also disordered by the genus *Lepidotus*, the teeth of which are far removed from the characters given to the families. It also differs from the other *Lepidoidei* in possessing a perfectly bony vertebral column, but it does not appear to belong to the *Pycnodontes* from the teeth. It is related to the *Lepisosteus* at present existing, both in the double rows of fulcra of the fins, and in the bony vertebral column.

The differences of the living Ganoids alone are perfectly accessible. This is so much the more important, as the two still existing ones, *Lepisosteus* and *Polypterus*, which are placed among the Sauroids, are so totally different from one another in external and internal structure, that they merit more than any one of the fossil ganoid genera to serve as types of particular families, as will appear from their anatomical structures. Finally, M. Agassiz has himself observed this difference in the osteological analysis of these fishes, and remarked that he was inclined to place them in separate families. Considering the perfect examination which these two fish admit of, and the marked differences which they present, I think that no two ganoid genera, possessing the structure of their scales, are more certainly distinct from one another.

In the conclusion of his great work, and in his recent monograph of the fossil fish of the old red sandstone, M. Agassiz has removed a large number of genera from the *Lepidoidei*, and formed them into separate families, as the *Cephalaspides*, *Acanthodei*, the true *Lepidoidei* and the *Dipterous Sauroidei*; this appears to me a decided advance. I have no doubt that the greater number of the *fossil* fish described and figured by Agassiz, and considered as Ganoids, really belong to a large order which includes *Lepisosteus* and *Polypterus*, and ranks as a group with the rest of the osseous fishes, the *Selachii* and the *Cyclostomi*; but I have never been able to convince myself that the other families of existing fishes enumerated among the Ganoids, the *Loricarini*, *Siluroidei*, *Lophobranchii*, *Sclerodermi* and *Gymnodontes*, belong to the Ganoids. Agassiz has in some degree perceived the difference of these fishes from the Ganoids of

the old formations and *Polypterus* and *Lepisosteus*; for he says (*Poiss. Foss.* ii. p. 11) "the relations of structure which connect the *Lepidoidei*, the *Sauroidei*, and the *Pycnodontes*, are more intimate than those which exist between these families and the *Sclerodermi*, the *Gymnodontes*, and the *Lophobranchii*."

The Siluroidei agree so perfectly in their anatomy with the Abdominal Malacopterygians, that they cannot be separated from them; they have merely the air canal of the swimming-bladder and the abdominal position of the ventral fins in common with the living Ganoids, characters which they also share with a large section of osseous fishes, which I shall call *Physostomi*, on account of their air canals, as the *Cyprinoidei*, *Esoces*, *Clupeæ*, *Cyprinodontes*, *Mormyri*, *Characini*, *Salmones*, *Anguillares*, &c. However, this air-passage is absent in the *Sclerodermi* and *Gymnodontes*, as also in many orders of osseous fishes; their ventral fins, when present, as in *Triacanthus*, are not abdominal; in both points they differ from the living Ganoids, and in the latter character from all true Ganoids. The Ganoids can only be accurately defined from the characters with which we have as yet become acquainted, ranging among them those fishes only which agree with *Lepisosteus* and *Polypterus* in the scales being covered with enamel. If we include the bony laminæ of the *Loricarini*, *Lophobranchii*, *Ostracion*, some *Siluroidei*, as *Callichthys*, *Doras*, and the prickles of *Diodon* among the Ganoid structures, all accurate definition ceases. For, first, we are obliged to admit the naked *Siluroidei* and the *Gymnodontes*, merely because some of their genera are covered with laminæ or prickles, and hence it becomes possible that families of Ganoids might exist, in which all the genera are unarmed, which would render separation and recognition impossible, as long as no essential characters of the Ganoids were known. Still greater confusion would be produced by those fishes belonging to other orders which have osseous carapaces, as the *Peristedia*, *Agoni*, and other *Cataphracti* with osseous laminæ, the nearest in relation to which are provided with scales, as the *Triglæ*; these however are not Ganoid scales. Finally, the scales of many *Sclerodermi*, as the *Monacanthi* and *Aluteres*, have but little resemblance to those of the Ganoids.

Should all these animals be left among the true Ganoids, their characters would be so confused, that it would be utterly impossible to say what would then constitute a real Ganoid, we

should be obliged to confess that the characters of this order are perfectly unknown, and the admission of many families among them would hence be more or less arbitrary.

The chief points in Agassiz's work, which is indisputably the most important ichthyological treatise of modern times, have been for some years before us. They have not hitherto been developed nor analysed by any philosopher in a proper manner. Wiegmann, in his report of 1835*, says of it, that the system, being based upon a *single* peculiarity of the organism, would give rise to the fear that it might prove rather an artificial than a natural system, and might occasion a doubt whether comparative anatomy would find as great an agreement among those comprehended in the separate orders, as it might require from the orders of a natural system. But no facts are placed before us so as to enable us to judge. And it must be confessed, that means for such an analytical development of the increase in ichthyologic information which has lately been acquired have hitherto been wanting.

I have been occupied for a long time with the anatomy of the *Polypterus*, and more lately of the *Lepisosteus*, endeavouring to ascertain the true characters of the order. I have succeeded, and I now think that I can positively prove,—

1. That the Ganoids form a well-defined order, between the true osseous fishes and the Selacians.

2. That Agassiz's view of the position of the Sturgeons among the Ganoids is correct.

3. That, on the other hand, the *Sclerodermi*, *Gymnodontes*, *Loricarini*, *Siluroidei* and *Lophobranchii*, do not belong to the Ganoids, but to the other osseous fishes.

4. That there are unarmed and scaleless fishes, the families belonging to which gradually pass into one another, without losing the true Ganoid character.

This is not the first time that *Polypterus* and *Lepisosteus* have been treated of. Geoffroy St. Hilaire has described the intestines of the *Polypterus* which he discovered; we have also papers on its osteology both from the same author, and more detailed ones from Agassiz. Agassiz has taught us the osteological peculiarities of *Lepisosteus*; Cuvier, Valentin and Van der Hoeven have examined its intestinal system. Although these communications are valuable towards our anatomical knowledge

* *Archiv f. Naturgesch.* 1 Jahrg. ii. p. 258.

of this animal, and essentially contribute to its explanation, still they do not contain certain facts, which directly relate to the question of the nature of the Ganoidei, nor of their relations and limits, and the determination of which is the object of this treatise. Moreover, all we know of the internal structure of these two fishes is referable to generic peculiarities, which occur in one of them, but are absent in the other. The anatomical characters of the Ganoidei are to be sought for in the structure of the heart, the blood-vessels, the respiratory organs, the sexual organs, the brain, and the organs of sense.

The first point to which I shall draw attention is the structure of the heart, or rather of the *bulbus arteriosus*.

I have long attended to the importance, in a systematic point of view, of the internal structure of the arterial trunk arising from the heart. We know, that in those osseous fishes in which it has been examined, only two opposite valves are situated at the origin of the muscular bulb, between it and the cavity, whilst the higher cartilaginous fishes, the Sturgeons, *Plagiostomi* (Rays and Sharks), and the *Chimæræ*, have three or more longitudinal rows of valves within the muscular bulb, the number in each row varying from two to five according to the genus. At that spot, opposite which the two valves of the osseous fishes are found, the former fishes have no valves.

The *Cyclostomi* are essentially different in this respect from both the higher cartilaginous and the osseous fishes. They resemble the osseous fishes in possessing only two opposite valves at the origin of the arterial trunk from the cavity, but they differ from both orders essentially by the muscular arterial bulb, or accessorial arterial heart being entirely absent. Their arterial trunk consists merely of the simple coats of the artery. This I found to be the case in both *Petromyzon* and *Myxine* *. These distinctions appeared so constant in all osseous and cartilaginous fishes which I have examined, that they seemed to indicate a fundamentally different disposition of the orders. I am unacquainted with any character, either anatomical or zoological, which equals this in its absolute certainty. In fact, if the Ganoidei are essentially distinct as an order from other fish, a marked difference must occur in this part.

* See *Vergl. Anatom. der Myxinoid.* 3 Forts. *Abhandl. d. Akad. d. Wissenschaft.*, J. 1839, p. 284; see also on the difference in the valves in the orders, families and genera, the note in *Archiv f. Anat. u. Phys.*, 1842, p. 477.

When I first examined the *Polypterus* on this point, I was much astonished on finding that this so-called osseous fish differed from all other osseous fishes in its valves, and that it agreed in that respect with the higher cartilaginous fishes, the Sturgeons, the Rays, Sharks and *Chimæra,* and far exceeds them in the number of valves. The *Polypterus* possesses no valve at the origin of its exceedingly long muscular bulb; but within it there are three longitudinal rows of valves, in each of which there are nine segments, which are connected by filaments, as in the Sturgeons and *Plagiostomi.* The uppermost are as usual the largest. Between the three complete rows of large valves there are three other longitudinal rows, the valves of which are less developed both in size and number, so that the perfect longitudinal rows alternate with the imperfect. Thus there are altogether six longitudinal rows. If the imperfect rows were as complete as the perfect ones, *Polypterus bichir* would have fifty-four valves in the muscular arterial trunk; there are in fact only forty-five present.

It was to be expected that this peculiarity would also be found in *Lepisosteus,* of which at first I had no specimen. I lately examined it in the Jardin des Plantes at Paris. *Lepisosteus osseus* has five equally developed rows of valves in the arterial trunk, in each longitudinal row eight perfect sacculated valves, connected by filaments. Those of the uppermost oblique rows are longer. The rows appear like the cups of a well-wheel or a machine for removing mud. No cartilaginous fish possesses so many valves as the Ganoidei spoken of. In the Sturgeon there are twelve only; and in the Rays and Sharks, where their number reaches its maximum, there are not more than fifteen present, as in *Raia, Myliobatis, Pteroplatea, Scymnus* and *Squatina.*

We have now discovered a character which removes the *Sclerodermi, Gymnodontes, Siluroidei, Goniodontes* and *Lophiobranchii,* distinctly from the Ganoidei, and refers them to the true vertebrated osseous fishes. According to my observations, all these fishes agree with the other osseous fishes in their organization; especially, as far as to the present point, they resemble all true osseous fishes, in the fundamental peculiarity of the arterial trunk being furnished with two valves at its origin. In the *Sclerodermi* I have examined the genera *Balistes* and *Ostracion*; in the *Gymnodontes* the genus *Tetrodon*; in the *Siluroidei* the genus *Calophysus,* M. T.; in the *Goniodontes* the genera *Hypostoma* and *Loricaria*; in the *Lophobranchii* the

genus *Syngnathus*. It will suffice to place the constancy of the valvular structure in all true osseous fishes beyond doubt, that types of thirty-five families of osseous fishes have been examined on that point, and that no deviation has ever been found. I have placed my observations with those of others in the subjoined table.

Osseous Fishes having two valves*.

Order.	Family.	Genus.
Acanthopteri	Percoidei	Uranoscopus, Trachinus*.
	Cataphracti	Scorpæna, Trigla*.
	Sparoidei	Dentex*.
	Sciænoidei	Umbrina.
	Squamipennes	Chætodon.
	Scomberoidei	Scomber, Zeus, Xiphias*.
	Tænioidei	Trachypterus*.
	Teuthyes	Naseus*.
	Labyrinthici	Ophicephalus*.
	Mugiloidei	Mugil.
	Gobioidei	Gobiesox*, Cyclopterus*, Echeneis*, Gobius.
	Blennioidei	Soarces*.
	Pediculati	Lophius.
	Fistulares	Fistularia.
Anacanthini	Gadoidei	Gadus, Macrurus*.
	Ophidini	Ophidium*.
	Pleuronectides ...	Pleuronectes.
Pharyngognathi ...	Labroidei cycloidei	Scarus*.
	Labroidei ctenoidei	Pomacentrus*.
	Chromides	Chromis*.
	Scomberesoces ...	Belone.
Physostomi	Siluroidei	Calophysus*, Loricaria*, Hypostoma.
	Cyprinoidei	Cyprinus.
	Characini	Erythrinus*.
	Cyprinodontes	Anableps*.
	Esoces	Esox.
	Mormyri	Mormyrops*.
	Salmones	Salmo.
	Scopelini	Saurus*
	Clupeidæ	Arapaima*.
	Murænoidei	Muræna.
Plectognathi	Balistini	Balistes*.
	Ostraciones	Ostracion*.
	Gymnodontes	Tetrodon*
Lophobranchi	Lophobranchi	Syngnathus*.

* Isolated and scattered observations exist in the writings of the older authors, as on the Salmon by Collins, the Swordfish by Bartholine, Walbaum, &c. The genus *Gadus* was examined by Cuvier; *Uranoscopus, Scorpæna, Umbrina, Chætodon, Scomber, Zeus, Mugil, Fistularia, Belone, Esox, Muræna, Gobius, Hypostoma, Pleuronectes* and *Salmo* by Tiedemann (*Anatomie des Fischherzens*), and *Lophius* by Meckel. The genera which I examined have a * affixed to them. As regards the orders in which the families are placed, I must refer to the development of the natural system of fish at the end of this treatise.

The grounds which should determine the removal of the above families from the Ganoidei, apply equally to the *Lepidosiren*, which was appended to the Ganoidei, from which it differs as much by the valves of the *bulbus arteriosus* as by the structure of its scales. Agassiz ascribes a layer of enamel to these scales; but in their mosaic structure they approach the compound scales of *Sudis* and *Osteoglossum*. They have no concentric raised lines, and are merely granulated and reticulated on the surface; but such elevated lines in the scales of osseous fishes imperceptibly pass into reticulations and granulations, as may be seen in the free portion of the scales of *Sudis* and *Osteoglossum*. I have never been able to find any enamel on the scales of the *Lepidosiren*.

I shall now turn to another important point in the organization of the Ganoids, the respiratory organs.

In my treatise on the accessory gills and pseudo-branchiæ, I have proved that the false accessory gills or pseudo-branchiæ with the function of a *rete mirabile* occur in the osseous fishes, as well as in the *Plagiostomi* and *Sturiones*; that, on the other hand, a true accessory gill, anterior to the first gill-arch, near the operculum, does not appear in any osseous fish, and characterizes the Sturgeons, which have this in common with the *Plagiostomi*, although in the *Plagiostomi* the operculum is wanting. It was also there pointed out, that the Sturgeons possess both the true accessory opercular gill and the pseudo-branchiæ, the latter existing in the blowing-cavity. This property of possessing a respiratory opercular gill is not peculiar to the Sturgeons as Sturgeons, but, as will now be shown, so far as they are Ganoids; for the Ganoids differ in this character from the osseous fishes, and approach the *Plagiostomi*, as they do also in the structure of the valves.

The intimate relation of the Sturgeons with the Ganoids remained long concealed from me, and I had not understood it, even at the time when I detected the numerous valves of *Polypterus*, as is evident from my report on Agassiz's *Poissons Fossiles* in the last *Jahresbericht*; for I then possessed the means of separating the *Scleroderми*, the *Gymnodontes*, *Siluroidei*, *Goniodontes* and *Lophobranchii* from the Ganoids; but the Sturgeons then appeared to me to be distinct from the Ganoids. This was necessarily established in the complete development of my ichthyological investigations. Thus in making observations

on the accessory gill as a peculiarity of the Sturgeon not existing in the other fish with an operculum and free gills, that fish was found to possess in addition a respiratory opercular gill, which was not then known to occur in any other fish having an operculum and free gills, nor in any Ganoid. It is also wanting in *Polypterus*, and I therefore had not, until that time, any sufficient ground for placing the Sturgeons and Ganoids together. Moreover, the *Spatulariæ*, which are inseparable from the Sturgeons, did not, in consequence of being unarmed, present any point of comparison with the Ganoids which were so very scaly. But when I had obtained an opportunity of examining *Lepisosteus*, and still found in it these same peculiarities of a respiratory opercular gill, the position of the Sturgeon among the Ganoids was clear and decided; and the peculiarity which I pointed out as existing in the Sturgeons only, of possessing an opercular gill, was now extended as a peculiarity naturally possessed by the Ganoids, but not occurring in true osseous fishes.

In *Lepisosteus* the respiratory gill of the operculum is present as well as a pseudo-branchia. The statement made by Valentin *, in his account of my investigations regarding the false accessory gills or pseudo-branchiæ of *Lepisosteus*, and considered by him as its internal and external accessory gills, is explained by the existence of a respiratory accessory gill as well as a pseudo-branchia. These two organs preserve the same relation as in the Sturgeons. I have proved their true importance by the investigation of their blood-vessels. The gill of the operculum of *Lepisosteus* is very considerable, and its upper end is joined at an acute angle to the pseudo-branchia, which is much smaller. Both organs, which as in the Sturgeons are of similar external structure, are in contact by their extremities, without adhering. The direction of the plates is opposite, at the point of contact. The muscular *bulbus arteriosus*, as in the Sturgeons and *Polypterus*, forms a very long trunk; its muscular structure suddenly terminates just behind the spot where the artery begins to divide. The artery then divides into an anterior and a posterior branch. Two branches arise from the posterior portion on each side, the anterior of which is the artery of the gill of the second gill-arch; the posterior again divides into the arteries of the third and fourth gill-arches. The anterior portion of the *truncus arteriosus* proceeds forwards, then gives off on each side

* Valentin, *Repert.* 1841, p. 137.

the gill-arteries of the first arch, and is continued in the middle line as a thinner trunk. This azygous continuation of the trunk of the gill-artery passes out of the region of the gills of the gill-arches, and forms the trunk of the arteries of the opercular gills of the right and left side. After a course of half an inch it divides into a right and left branch, which direct themselves towards the internal surface of the membrane of the gills, and run between the mucous membranes as far as the operculum and its gill. The membrane of the gill in *Lepisosteus* passes uninterruptedly in the form of a broad mantle from one side to the other, and is provided with an equally broad layer of transverse muscular fibres.

In the Sturgeons, the continuation of the gill-artery to the first gill-arch also gives the artery of the gill of the operculum *. Hence the opercular gill of the Ganoids, like the true gills, contains dark red blood from the common arteries of the gills.

The artery of the pseudo-branchia is exactly the reverse of this; it does not arise from the gill-artery, it belongs to the arterial system of the body, and thus conveys bright red blood to the pseudo-branchia totally different from a respiratory organ, just as the arteries do to all parts of the body. In *Lepisosteus*, as in other fishes, it is a continuation of the arterial system, a *ramus opercularis*, which supplies the bones and muscles of the operculum. In *Lepisosteus* it is seen through an aperture opening internally in the same place, as in the osseous fishes. I have never been able to trace its origin from the first gill-vein, which I have proved to occur in other fishes, from not having specimens, but there is no doubt that its relations are the same.

The Sturgeons are distinguished from all other osseous fishes by their pseudo-branchia forming, as in the *Plagiostomi*, a *rete mirabile caroticum* for the eye and brain, whilst in all other osseous fishes a *rete mirabile ophthalmicum* alone exists. For reasons comprised in what I have stated above, the same may be imagined to occur in *Lepisosteus*. I must leave this question undecided until new specimens can be obtained.

The existence of an accessory opercular gill is incompatible with the nature of an osseous fish—it is a character of the Ganoids; but it is not necessarily peculiar to them. In the naked *Spatulariæ* most nearly related to the Sturgeons, as in *Planirostra*

* See *Anatomie der Myxinoiden*, 3te Fortsetzung.

edentula, Raffinesque, I find no opercular gill, but merely a pseudo-branchia concealed in their blowing cavity, which occupies the same position as the pseudo-branchiæ in the Sturgeons. *Polypterus* bears the same relation to *Lepisosteus* as the *Planirostræ* do to the Sturgeons. Like *Planirostra*, *Polypterus* possesses no opercular gill, and even the pseudo-branchia has here disappeared, only the blowing cavity has remained, in which I can recognise no trace of this organ. The occurrence of the pseudo-branchia is also subject to similar variations in the *Plagiostomi*: for I have not found it in several genera, as *Scymnus*, in which however at an early period of fœtal existence I have seen it in this situation*. The same applies to the blowing-hole. They are peculiar to most of the *Plagiostomi*, and, according to the above detailed observations, perhaps to all without exception in a fœtal state; but in the adult state they are wanting in the genera *Carcharias* and *Sphyrna*. The same relations are repeated in the Ganoids. The Sturgeons have blowing-holes: in the nearest related genus, *Scaphirhynchus*, Heck., the blowing-hole has disappeared. It is present however in the *Spatulariæ*: in *Planirostra edentula* it is a small aperture, equidistant from the eye and from the angle of the mouth. The *Polypterus*, as is well known, also possesses blowing-holes, but they are absent in *Lepisosteus*. Hence as regards the opercular gill, the pseudo-branchia and the ejecting-hole, almost all the combinations which are logically possible occur among the Ganoidei:—

1. Opercular gill, pseudo-branchia and blowing-hole—*Acipenser*.

2. Opercular gill and pseudo-branchia without blowing-hole—*Lepisosteus*.

3. Opercular gill without pseudo-branchia and without the blowing-hole—*Scaphirhynchus*.

4. Pseudo-branchia without opercular gill but with blowing-hole—*Planirostra*.

5. Blowing-hole without opercular gill and without pseudo-branchia—*Polypterus*.

The presence of the blowing hole is no absolute character of the Ganoids, for *Lepisosteus* forms an exception even among those now in existence, but the negation of this character is absolute

* *Vergl. Anat. der Myxinoiden*, 3 Fortsetzung. *Abhandl. d. Akademie d. Wissenschaft.*, 1840, p. 252.

in the case of the true osseous fishes. The existence of the blowing-hole in *Polypterus* was an incomprehensible fact so long as it was considered as an osseous fish. Now, since it has been proved that the Sturgeons and *Spatulariæ* are most closely related to it, the reverse happens; it rather requires to be explained why these openings, which appear to be so essential to the constitution of a Ganoid, are absent in *Lepisosteus*. I believe that they occur in it in the fœtal state, just as I found them in the fœtus of those genera of Sharks, in the adult state of which they are absent (*Carcharias*).

The swimming-bladder is present in all the living Ganoids, as well as the Sturgeon and *Polyodon*; it is furnished with an air-duct, but not with a *rete mirabile*, as in the Abdominal Malacopterygians, or more certainly the *Physostomi*, among the osseous fishes.

The relations of the sexual organs in the Ganoids are very peculiar. The account of the sexual organs of *Polypterus* in the *Description de l'Egypte*, is imperfect and partly incorrect; in pl. iii. fig. 7, *tt*, the fatty valves of the chylopoetic viscera are mistaken for testicles.

The ovaries of *Polypterus* lie anterior to the kidneys in the form of a long plate: each is attached to a mesentery. They have no internal cavity, and there is no outlet from them except into the abdominal cavity, as we find in the *Plagiostomi*, the Sturgeons, *Cyclostomi*, and a few osseous fishes, such as the Eel and Salmon. The ova are conveyed from the abdomen through true oviducts. This entirely separates *Polypterus* from the osseous fishes, also from those last-mentioned, in which there is a mere abdominal aperture without any oviduct; it rather approximates to those fishes which have separate oviducts, viz. the *Plagiostomi*, Sturgeons and Lepidosirens. The form of the oviduct most nearly resembles that of the Sturgeons.

In *Polypterus* the oviducts are situated exactly in front of the long and broad urinary tubes, and are united to them by fibrous tissue; they open into the abdominal cavity at the distance of a few inches from the anus, by a broad transverse slit. This orifice lies close to the ovarian mesentery, externally to its under side. The oviduct and ureter follow their course, remaining separate until just before the common termination in the urogenital pore behind the anus. If we inflate the latter, the ureters become gradually filled with air, sometimes also the oviducts.

If we blow into the abdominal aperture of the oviduct, the air rushes out at the urogenital pore.

In the Sturgeons, the form and position of the abdominal orifice of the tube are exactly the same. But the tube at this point is isolated for a short distance only, it soon terminates in the broad ureter which then at the same time becomes an oviduct. In male sturgeons the same infundibulum leads from the abdominal cavity to the oviduct. M. v. Baer was the first who described this interesting fact in the anatomy of the male organs of generation of the Sturgeon*. M. Rathke† has proved its existence in females. Whilst examining this point I met with one circumstance which had been overlooked by these two anatomists. The infundibulum leading from the abdominal cavity to the ureter appears in the ureter as a blind sac; in many large sturgeons, both male and female, these broad sacs were perfectly closed, so as not to allow the passage of air or mercury. This object being so large, a blind pouch of the diameter of the little finger, an error is hardly possible. In one case, among many, the funnel-shaped canal did not form a blind pouch, but opened into the ureter. It was in the male generative organs which had been removed from a very large sturgeon, and had been made into a preparation a long time previously; I also found the infundibulum open in the ureter of a female *Scaphirhynchus Raffinescii*, Heck.; in both cases it was open on each side. Hence it appears that the abdominal infundibula are only open at certain times, at others remaining closed. A large female, in which the blind pouch of the infundibulum was closed, was found in the summer in the river Oder, the ovary contained immature ova perceptible with a lens‡.

The Sturgeons have also on each side of the anus an abdominal orifice; this is wanting in *Polypterus*, as also the communication between the cavity of the abdomen and the pericardium; the pericardium exhibits merely a deep depression towards the posterior part. In general the outlet of the anus is anterior to that

* *Berichte der K. Anatom. Anstalt zu Königsberg*, ii. Leipzig, 1819, 40.

† *Ueber den Darmkanal und die Zeugungsorgane der Fische.* Halle, 1824, p. 124.

‡ The manner in which the seminal fluid is excreted is still unknown. Rathke thought that he discovered oblique canals between the testes and the urinary tubes in the Sturgeon. The testes certainly consist of twig-shaped seminiferous tubes, which may be seen with the lens, and not of minute vesicles; but they are very confused, and their arrangement and mode of termination still remain unknown to me.

of the *porus uro-genitalis* in both animals, as in the osseous fishes, and different from the cloaca of the *Plagiostomi*.

The Ganoidei approach the *Plagiostomi* in the formation of the alimentary canal, for *Acipenser* and *Polyodon* have a spiral valve in the intestine, as in the Sharks and Rays, and in *Polypterus* it has been described by its discoverer, but no osseous fish possesses such a structure. The spiral valve, however, is not universal among the Ganoids, for it has not been shown to exist in *Lepisosteus*. The intestine of the *Plagiostomi* and *Polypterus* is formed on the same plan. The tube which ascends from the sacciform stomach, which in this instance passes off laterally, extends as far as the valvular intestine, where we first meet with the pylorus. This tube is therefore not an intestine, as Geoffroy St. Hilaire called it, but the ordinary pyloric canal, the "*branche montante*" of the stomach. At the upper rounded end of the valvular intestine of the *Plagiostomi* a valveless cavity exists between the commencement of the valve and the pylorus. This is the *bursa Entiana*; it receives the biliary and pancreatic ducts, and also in the fœtus the *ductus vitello intestinalis*; it is undoubtedly that portion of the small intestine which most nearly resembles the duodenum. If the valvular intestine be considered as the colon, this would receive nothing more from the small intestine than the *bursa Entiana*, which is absurd. The entire valvular intestine with the *bursa* ought rather to be considered as the small intestine, and the valveless end of the rectum alone as analogous to the large intestine. In the osseous fishes, likewise, the canal is not divided into small and large intestine, but into small intestine and rectum. The intestinal canal of *Polypterus* may be explained in this manner, or rather the intestine of this Ganoid itself confirms this view. In *Polypterus* a *bursa* is barely perceptible, and the valve of the valvular intestine arises from the circumference of the pyloric infundibulum. Near this spot the intestine expands into the blind, sacciform appendage, called the *appendix pylorica*, and the biliary duct also opens near the pylorus. Had Geoffroy St. Hilaire sought for or known this orifice, he would not have considered the pyloric duct of the stomach as the small intestine.

The Sturgeons differ from *Polypterus* merely in the form of the stomach, and in the development of the space between the valve and pylorus or the *bursa* of the *Plagiostomi*, which forms a complete flexure, the duodenal loop of the intestine. Their

stomach has no blind pouch, the pyloric portion forms an unlimited number of curves, and after a muscular swelling constitutes the pylorus. The duodenal loop comes next; this receives the terminations of the appendices, the biliary duct, and the duct of the glandular pancreas discovered by Alessandrini; the lower extremity of this forms another valve, from the circumference of which the spiral valve of the valvular intestine takes its origin. The Rays form the transition from *Polypterus* to the Sturgeons; their *bursa Entiana* is prolonged towards the pylorus in the form of a retort-like canal, so that the pylorus does not open into the body of the *bursa*, but projects into the neck of the retort.

The brain of the Ganoidei is peculiar, and differs from that of the osseous fishes and *Plagiostomi*. That of the Sturgeons is well known from the treatise by Stannius. I shall now give a short account of the brain of *Polypterus*. It resembles that of the Sturgeon, and consists, at its posterior part, of a very elongated medulla with the long *sinus rhombicus*, a cerebellum, and comparatively small optic lobes, which terminate with a superior aperture in the *lobus ventriculi tertii*. Next follow the very large and deeply-divided hemispheres, and not olfactory lobes, as I called them in the *Jahresbericht*. The brain is continued beneath them in the form of the olfactory lobes and the olfactory nerves. The decussation of the optic nerves found in osseous fishes is wanting; they do not pass over each other in an isolated state, but are united and form a chiasma as in the Sturgeon. The skull of *Polypterus* has a very considerable mass of cartilage beneath the bony coating, which partly incloses the auditory apparatus on each side, so that the latter is somewhat more covered than in the osseous fishes, which again reminds us of the Sturgeons.

In the organs of sense, the Ganoids partly approximate to the osseous fishes, partly to the *Plagiostomi*. They have, like the Sturgeons, double nasal cavities, which do not occur in the *Plagiostomi*. The *processus falciformis* and the choroid glands appear to be wanting in *Polypterus*.

The skin of the Ganoids may either be covered with rhomboidal or round enamelled scales, it may bear plates, or be perfectly naked. The *Spatulariæ* are naked sturgeons, their intestines and vertebral column are the same; the imperceptible transition of the Sturgeons to the Ganoids generally is easily recognised,

even in the cutaneous covering. In the true Sturgeons the large osseous plates are placed in longitudinal rows, which are separated by a considerable interval in *Scaphirhynchus*; the posterior part of the body is uniformly covered with ganoid plates. But the ordinary Sturgeons likewise possess true ganoid plates at the sides of the tail. Moreover, the *fulcra* of the summit of the elongated upper tail-piece are as in *Palæoniscus*, *Acrolepis*, &c. No one who saw the tail only of a sturgeon would hesitate to pronounce it to be the tail of a heterocercous Ganoid.

Taking all things into consideration, the only true Ganoids of the present time are the genera *Polypterus*, *Lepisosteus*, *Acipenser*, *Scaphirhynchus*, and *Spatularia*. This result, independently of its immediate interest, is also remarkable, because it relates to the fish with which Cuvier compared *Palæoniscus* in 1824. It was not this great philosopher's intention to place the Sturgeons, *Polypterus* and *Lepisosteus*, in one section with the *Palæoniscus* of the Zechstein; it may rather be proved that this idea was entirely foreign to his mind. In 1828, in the new edition of his 'Animal Kingdom,' he has still arranged the Sturgeons in his section of cartilaginous fishes, *Lepisosteus* and *Polypterus* among his osseous fishes, in the abdominal Malacopterygian family of the *Clupeæ*. His idea, which he expressed in definite words, was simply that the *Palæoniscus* should *either* be united with the *Lepisosteus* and *Polypterus*, *or* with the Sturgeons; that the determination of this depended upon certain doubtful points; and he inclined to the opinion, which was more distinctly expressed by Valenciennes, that *Palæoniscus* and *Dipterus* belonged with *Lepisosteus* to the abdominal Malacopterygians.

The characters of the Ganoids when summed up are the following:—They are fishes provided with either tabular and angular or round enamelled scales, or with bony plates, or a perfectly naked skin. Their fins are frequently, but not always, covered on their anterior border with a single or double row of spiny plates or laminæ. Their caudal fin sometimes receives in its upper fold the extremity of the vertebral column, which may continue as far as the extremity of that fold; their double nasal apertures resemble those of the osseous fishes; their gills are free and lie in a gill-cavity covered by an operculum, as in the osseous fishes. Several have an accessory respiratory organ in the form of an opercular gill, which must be distinguished

from a pseudo-branchia, and may occur at the same time with it; many have also blowing-holes, as in the *Plagiostomi*. They have several valves in the arterial trunk like the latter; their *ova* are conveyed from the abdominal cavity by tubes; their optic nerves do not pass over one another in a cruciform manner; their intestine often contains the spiral valve of the *Plagiostomi*; they have a swimming-bladder with an air tube like many osseous fishes; their skeleton is either bony or partly cartilaginous; and their ventral fins are abdominal.

When, however, we form those characters only which are absolute and never absent into a definition, the Ganoids are in fact *those fishes which have numerous valves in the arterial trunk, no decussation of the optic nerves, free gills and opercula, with abdominal ventral fins.* The skin and scales with which we commenced our investigation are not included. I consider the character of the abdominal ventral fins merely as a temporary link.

Among the fishes considered by Agassiz as Ganoids, there are fortunately but few from families which are now certainly known to be common osseous fishes. *Acanthoderma, Pleuracanthus, Diodon, Ostracion,* and *Calamostoma,* positively belong to the true osseous fishes, the last genus as a Lophiobranchiate, the others as *Plectognathi.*

As the fossil genera *Blochius, Dercetis* and *Rhinellus,* have little or no resemblance to the *Sclerodermi,* to which they are referred in the *Poissons Fossiles,* it becomes a question whether they should not be retained among the Ganoids. *Blochius,* according to Agassiz, has rhomboidal enamelled scales, but the probable position of its ventral fin near the thoracic fin renders their ganoid nature doubtful. Rhomboidal scales alone afford no positive character, for *Balistes* have them without being Ganoids. As regards the enamel, I consider this of value on small scales only, when no other characters are opposed to the ganoid structure; the existence of enamel was also ascribed to *Balistes,* but this I cannot admit. A more accurate knowledge of the position of the ventral fin in *Blochius* will assist us materially on this point. The osseous plates of *Dercetis* and *Rhinellus* would not be sufficient to prove them to be Ganoids; for such plates exist in many osseous fishes, and in others which do not possess them in the adult state they sometimes occur in the young, as in the Sword-fish.

Be this, however, as it may, whether *Blochius, Dercetis* and

Rhinellus, are Ganoids or not, this question has no more influence on the geognostic deductions than the separation of the false Ganoids, viz. the *Plectognathi* and *Lophobranchii*; for, after all, it refers to fishes which are subsequent to the Jura formation: the hitherto assumed relations of the fish to the age of the formations are not thereby affected. Agassiz has advanced the opinion that the Ganoids predominate in the older formations, that, leaving out the Placoids, all the fish prior to the Chalk formation are Ganoids, and that true osseous fishes commence with the Chalk. This conclusion is not in the least shaken, and must be considered as approximating to the truth. But the state of preservation of fossils makes us feel that much is wanting, in particular instances, for the proof to be absolute. The deductions as to the relation of the Ganoids to the formations are merely changed by our investigations in reference to the formations beginning with the Chalk, and the development of the Ganoids in all newer formations, as well as in the existing creation, is considerably reduced by the removal of the foreign families.

With existing fish we can decide with absolute certainty, from their anatomy, whether they are Ganoids or not. But what characters are to guide us with respect to fossil fish? In the first place, we have enamelled rhomboidal scales articulated with each other by appendices and arranged in oblique rows, spinous plates (*fulcra*, Agass.) on the anterior border of one or more fins, heterocercy in a fish furnished with an operculum, an abdominal position of the ventral fins and soft articulated fin-rays. Where *fulcra* exist on the borders of the fins, I consider the ganoid nature of a fossil as decided, whatever the form of the scales, for this character is not found in any other fish. The perfect heterocercy in a fish having opercular and cephalic bones is equally decisive, for these are not found except in the *Plagiostomi*. The covering of the margin of the fin with *fulcra* is widely diffused, and may sometimes be overlooked, although present. I find it among several specimens of the great *Pachycormus macropterus* of the Lias slate, in one instance perfectly distinct, both on the dorsal fin and the anal fin; whilst on the tail fin it is absent in all. However, in many genera the *fulcra* appear to be entirely wanting; and that this is both possible, and does actually occur, we find a distinct proof among those at present existing in *Polypterus* and *Polyodon*. Although the vertebral column of

the Ganoids is frequently osseous, still the unossified condition of the central portion, where the apophyses are barely ossified, is an important sign where any part of the above most important characters are absent. The mere rhomboidal form of the scales without any peculiar enamel, without articulations, with fulcra on the margins of the fin, without heterocercy, with an ossified vertebral column, and still more so where the ventral fins are wanting, or not placed on the abdomen, would be doubtful, as is the case with *Balistes*. But even when other characters are wanting, if the scales be articulated, as in *Gyrodus*, there appears no room for doubt. With respect to several Ganoids, Agassiz does not bring forward complete proofs why they are Ganoids. A long acquaintance with his work however creates great confidence in his experience on this point. We are satisfied as regards the *Cœlacanthi*, when we see them with their round, imbricate scales figure among the Ganoids, as soon as we find that the apophyses only of their spine, not its central portion, is ossified, as is met with so distinctly in *Undina*. The age of the formation may also be taken into account, to a certain extent, in arranging a fish among the Ganoids. But this indeed is already a *petitio principii*.

The osseous substance of the scales of *Lepisosteus* and *Polypterus*, when microscopically examined, exhibits the radiating osseous corpuscles as they exist in the bony plates of other fishes, but which do not usually occur in the ordinary scales of the osseous fishes. In very large scales, however, even of osseous fishes, a lowermost layer containing osseous corpuscles is sometimes met with. I also find them in the scales of *Sudis*, which do not otherwise differ from those of other osseous fishes. In the genera *Megalurus* and *Leptolepis*, from the upper member of the Jura formation,—the lithographic slate,—we are reduced in their determination to the consideration, that their round, imbricate scales, without osseous corpuscles, which appear similar to the scales of the osseous fishes, are covered with enamel, and that they belong to the Jura formation. On a microscopic examination of these scales, I find the concentric lines as in the scales of the osseous fishes, but they are really covered with a thin vitreous layer of enamel, so that they usually leave no impression of the lines on the stone. I am uncertain what position should be assigned to this fish.

As there exist among the living Ganoids some which are

naked, so do some such undoubtedly occur among those which are fossil; these could not be recognised from the structure of the surface of the body, but from their affinities to other genera only, and partly from the condition of the vertebral column.

The cartilaginous structure of the central portion of the vertebral column alone will not positively decide whether a fish furnished with scales be a Ganoid; for we have in *Lepidosiren* an example of a group of scaly fish distinct from the Ganoids, provided with a cartilaginous centre to the vertebral column.

I now come to the systematic arrangement of the Ganoids. In the first place, we must admit that they form one of the largest divisions of fish, whether they be considered as an order or subclass, and that they do not merely constitute a single family. As long as the peculiar differences in the anatomy of the Ganoids from that of the osseous fish, as in the structure of the valves, the optic nerves, the respiratory organs and the organs of generation, were unknown, the position of those fish which agreed with *Lepisosteus* and *Polypterus* in the structure of the scales was doubtful, whether they constituted an order or a family of the Malacopterygii Abdominales. For if the *Lophobranchii*, *Gymnodontes* and *Sclerodermi* were separated from the Ganoids, the latter agree with the Malacopterygii Abdominales in the possession of the air-duct of the swimming-bladder, the position of the ventral fins, and the soft structure of the fin-rays. For this reason, in my treatise on the natural families of the osseous fish, I left *Lepisosteus* and *Polypterus* in the order in which Cuvier had placed them, *i. e.* among the abdominal Malacopterygians, but as a separate family. In the present state of my knowledge this is inadmissible. It is evidently proved that these fish fundamentally differ from the osseous fishes. They have equally little claim to be arranged among the *Selachii*; at the same time, as they approximate to one portion of the previous cartilaginous fishes, they form a separate section. The systematic position of this section, as I think I have proved, lies intermediate between the osseous fishes and *Plagiostomi* or *Selachii*, combining the characters of the osseous fishes and the *Selachii*. It has the gills, the opercula and the snout of the former, and the accessory gill to the first gill, the blowing-hole, the valves, the vascular subdivision of the pseudo-branchia, the oviduct and the structure of the optic nerve of the latter.

It may be stated that some animals in this section approximate

to the Reptiles in one or two points of their organization. I have never been able to convince myself that they are related to them more than any other fish, and that they form a transition to the Saurians. I find merely combinations of the properties of the osseous fishes and of *Plagiostomi* united in a third distinct form. The double vomer in *Lepisosteus* (Agassiz), and the connexion of its vertebræ by articular heads and sockets (Blainville), are decidedly remarkable in fish, and this certainly is a combination of forms which are next met with in Reptiles. Nor do these less frequently exhibit the peculiar spinal formation of fish with double excavated facets, as the *Ichthyosauri*, *Plesiosauri*, and the fish-like Amphibia, &c., and the *Proteidea*, *Derotreta* and *Cæcilia*. The composition of the lower jaw of *Lepisosteus* of as many pieces as in the Reptiles (Geoffroy St. Hilaire), which is not repeated in *Polypterus*, I find in a decidedly osseous fish, *Osteoglossum*. The reception of the apophyses of the vertebræ into cavities in *Lepidotus*, M. Agassiz considers as characteristic, and with this exception peculiar to the Placoids, reminding us of the *Ichthyosauri*. It would be superfluous to compare this structure with that of the spine of the *Cycloidei* and *Ctenoidei*, as this insertion never occurs in the latter. I must remark here, that it actually occurs in many families of osseous fishes, as in the *Cyprinoidei*, *Salmones*, *Esox* and *Elops*. The only fishes which decidedly approximate to the Reptiles, are those which possess at the same time lungs and gills and perforated nares: *Lepidosiren* is to fish what the pisciform *Protei* are to the Amphibia. Isolated affinities always occur; but we likewise meet with them in other orders: in the sexual organs the *Plagiostomi* agree most with the other Vertebrata, *i. e.* come nearest in this respect to the Reptiles, and differ completely from the type of the ordinary osseous fishes, in their oviduct and accessory testicles.

By separating the *Lophobranchii*, *Gymnodontes*, *Sclerodermi*, *Goniodontes* and *Siluroidei*, the present section of the Ganoids becomes very considerably reduced, perhaps to a half; nevertheless the name Ganoid must be retained for the remainder as a subclass order of fish, not merely because this residue still contains the greater portion of the fossil Ganoids, and the separate families are but little, and partly not at all represented in the strata of our globe, but still more on account of the great merit which Agassiz has earned by his foundation of the Ganoids

and description of their fossil forms, and which are of such a kind that this philosopher's name must ever remain connected with the history of the Ganoids. As regards the subdivision of the *living* Ganoids, they are most naturally distributed as follows:—

I. Holostei.	
Family 1. *Lepidosteini.*	Genera *Lepisosteus.*
... 2. *Polypterini.*	... *Polypterus.*
II. Chondrostei.	
Family 3. *Acipenserini.*	Genera *Acipenser, Scaphirhynchus.*
... 4. *Spatulariæ.*	... *Polyodon,* Lacép., *Planirostra,* Raff.

The first have an osseous vertebral column, in the latter the skeleton is partly cartilaginous, and the vertebral column contains a soft chorda instead of vertebral bodies. Both are related to one another in the same manner as the *Selachii* and the *Chimæræ* among the *Plagiostomi.*

Lepisosteus and *Polypterus* exhibit so many differences, both internal and external, that they cannot remain united in the same family.

Lepisosteus.—Its upper jaw is composed of several pieces. The vomer is double. The lower jaw contains as many pieces as in the Reptiles; its vertebræ are articulated by articular extremities and sockets*. The nose is situated at the extremity of the much-elongated jaw, and contains the ordinary nasal folds, which are arranged simply. It has a respiratory opercular gill as well as a pseudo-branchia, but no blowing-hole. The gills on the four gill-arches are perfect, *i. e.* bifoliated, and behind the last arch and the hyoid bone there exists as usual a fissure. The gill-membrane passes over from one side to the other in the form of a mantle, is undivided, and contains three rays. The anterior margin of all the fins is covered with two rows of spinous scales. The fin-rays are all articulated. The caudal fin is abruptly truncate; its rays are inserted partly at the posterior extremity of the vertebral column, partly beneath it. The stomach has no blind pouch. In the pylorus there are several short blind in-

* The osteology of *Lepisosteus* is extremely well treated of by Agassiz in his *Poissons Fossiles,* t. ii.

testines*; there is no spiral valve in the intestine. The swimming-bladder is cellular, and contains *trabeculæ carneæ* between the cell divisions†: it opens by a long slit into the upper wall of the throat. The *trabeculæ carneæ* are not the cause of the cellular structure, as usually supposed; on the contrary, I find that the arrangement of the fleshy fibres is caused by the cellular structure of the walls; for the muscular structure of the fibres between the cellular spaces entirely ceases at a certain point, and the areas lying between them do not possess any subsequent evidence of muscular structure in their dividing lines (fibres)‡. The termination of the muscular structure on the fibres, in those which possess it, is very distinctly perceptible. This view is opposed by the cellular structure of the swimming-bladder in other fishes, in which no *trabeculæ carneæ* occur. The same occurs in the *Erythrinus* and some *Siluroidei*, and which have been elsewhere described. *Amia calva*, which I have recently examined on this point, should also be included.

Polypterus.—Its upper jaw is not divided into pieces, the vomer is simple, the lower jaw has the ordinary number of osseous pieces found in fishes, and the whole skull differs altogether but little from that of other fishes; at the angle of the mouth it possesses a labial cartilage supporting the upper and lower lips. The vertebræ on each surface are furnished with excavated facets, but no articular processes or sockets§. The opercular gill is wanting, no pseudo-branchia ever occurs, but they are provided with a blowing-hole on each side covered with an osseous valve. The fourth gill is composed of one leaf, and there is no fissure behind it; the *ossa pharyngea inferiora* are also wanting. The gill-membrane is cleft in the middle, and instead of any rays to the gill-membrane, there are merely a few osseous plates on each side. Along the back there is a perfect row of separate fins, each of which consists of a prickle and a fin-feather of articulated rays attached to its posterior surface, no other example of

* Valentin says the portal appendages are situated at the junction of the duodenum with the small intestine (*Repert.* 1840, p. 397). In this case the pyloric tube of the stomach is called the duodenum.

† See Valentin, *l. c.* 392. V. d. Hoeven, Mull. *Archiv*, 1841, p. 224.

‡ In the specimens from the Paris collection which I examined the intestines had been removed from the abdomen, but a small portion of the swimming-bladder was left behind, which was sufficient for the examination of the cells.

§ On the osteology of *Polypterus*, see Geoffroy St. Hilaire's *Description de l'Egypte*. Agassiz, *l. c.* ii. 2, 32, and Müller in *Jahresbericht Archiv*, 1843, p. ccxl.

which occurs among the Ganoids. The rounded caudal fin and the anal fin consist of articulated rays. Those of the caudal fin are placed both above and below the spine. The anterior margins of the fins are not covered with spinous plates. Of the fins, the pectoral and ventral fins are remarkable, the former for a scaly somewhat elongated limb; and its posterior surface, which differs from all the other fins, is covered with very small scales between the fin-rays; the ventral fins, by the peculiar character of containing the bones of a middle foot in addition to the fin-rays. The lingual bone is composed of three parts; its body, which receives the gill-arches, is very large and simple. Beneath the lingual bone, where in other fishes the hyoïdal keel projects against the clavicle and is immediately combined with it, in *Polypterus* there are two bones, one on each side; they are fixed between the middle and the most inferior portion of the horn of the tongue-bone. These bones are attached by ligaments to a third isolated piece, which connects them with the clavicle. The nose has a more complex structure than that of any other fish. In the large cavity, which is covered by the true nasal bones, is situated a labyrinth of five nasal passages; these are parallel to an axis, and thus form a prismatic elongated star. Each of these canals contains in its interior the gill-like arrangement of folds, which only occurs in one other instance amongst fishes. The anterior nasal aperture is prolonged into a membranous tube, the posterior is a small cleft in the cutaneous tegument anterior to the eye. The stomach forms a blind pouch, the pylorus a blind intestine; below the pylorus the intestine contains the spiral valves. The swimming-bladder is double, and consists of two unequally long sacs, that anteriorly coalesce into a short common cavity, which opens in a different manner from that of all other fishes, as I have elsewhere shown, not into the upper wall of the throat, but, like a lung, into the ventral wall, by a long fissure. However, these organs are not lungs, for they receive bright red blood, like all other parts of the body, from their artery, which is a branch of the last gill-vein, which itself proceeds towards the sac of the swimming-bladder. The veins of the swimming-bladder unite with the veins of the trunk, viz. with the hepatic veins. These sacs are not cellular, and are covered in their entire circumference by a muscular tunic.

The second section of the Ganoids contains the Sturgeons with only partial osseous spinal columns. Artedi, Gronovius

and Cuvier, united them with the *Cyclostomi* and *Plagiostomi* to form a large section of the Chondropterygii.

The difference of the osseous or partly cartilaginous skeleton is of but little importance when applied to the order of the Ganoids, as is evident from Agassiz's fossil Ganoids. But in subdividing the Ganoids, it appears to me to be very important; at least it is so with the *Selachii*. For the Sharks and Rays, in which the vertebræ are perfectly divided, and the *Chimæræ*, in which there is a *chorda dorsalis*, form groups which are in other respects remarkably distinct, although they are inseparable from the *Selachii*. In a treatise on the vertebral column of the *Plagiostomi*, which was undertaken for Agassiz's *Poissons Fossiles*, and is published in the second volume of that work, I have pointed out others which have a soft cartilaginous vertebral column in addition to the Sharks, which possess an osseous vertebral column. In them these cartilaginous bodies of the vertebræ are separate in the column of the spine, and the *chorda* is wanting; but the *Chimæræ*, on the contrary, really possess a true chorda.

The *Acipenserini* and *Spatulariæ* are principally distinguished by the skin, which is naked in the latter, and by the formation of the mouth, the jaws, and the opercula*. Opercula are also absent in the *Spatulariæ* (*Planirostra*). Their intestines are the same.

In the scales, the fossil Ganoids have more similarity to the living *Holostei* than to the Sturgeons; however, in the structure of the osseous or partly cartilaginous vertebral column, the former and the latter forms recur; it is difficult to arrange them among the living forms, because we are obliged to mix the positive facts of the anatomy of the living forms with those partially suspected of the fossil. In addition to *Lepisosteus*, according to Agassiz, we find numerous Lepidoid and Sauroid forms, which resemble it in the structure of the fins, having two rows of fulcra, and also in the completely ossified vertebral column, as *Lepidotus*, &c. But I am not acquainted with any analogue of *Polypterus* among all the fossil Ganoids, so that it appears to be even among them the type of a peculiar family. I consider the *Cœlacanthi*, *Pycnodontes*, and the families of the *Cephalaspides*, *Acanthoidei*, and *Dipteri*, which have been lately formed by Agassiz, as well-marked families, excepting perhaps the placing *Cheirolepis*

* See my *Vergl. Osteologie d. Myxinoiden.*

among the *Acanthoidei*, from which it appears to differ both in the absence of the spines as also in the possession of the fulcra.

I consider the separation of the *Lepidoidei* and the *Sauroidei* as artificial. But among the number of genera contained in them, there are several which have evident affinities to one another, and might afford grounds for separation. Agassiz himself has lately commenced so doing, as the *Acanthoidei*, *Cephalaspides* and *Dipteri* are principally taken from the *Lepidoidei*. But I do not know how it is possible to distinguish the remaining *Lepidoidei* from the *Sauroidei* by essential characters. It appears to me that if the Ganoids be formed into one family, they must agree in the condition of the spinal column as to whether it is osseous or its central portion cartilaginous. It then appears to me that those fossil Ganoids which are always evidently without fulcra to the fins belong to one group, and those in which they are constantly present to another. Among those Ganoids which are furnished with fulcra at the anterior margin of some or of all the fins, there are again essential differences in the structure of the fulcra, and such as appear to me systematically important. In the examination of well-preserved specimens I obtained the following results.

When the summit of the elongated upper tail-piece is covered with spines, they always appear to form a single row as far as the extremity; this is the case in the Sturgeons, and also in *Palæoniscus* and *Acrolepis*. The appearance of the fulcra in the first tail-fin of a heterocercous Ganoid does not necessarily imply that the anterior margin of the inferior piece and other fins should possess fulcra, for they are absent in the Sturgeons. The fulcra on the entire summit of the fin, where there are no rays, must be considered merely as a covering of scales in general, not as the fulcra of the fin-rays; hence a heterocercous Ganoid, which possesses simple fulcra on the summit of the elongated upper tail-piece, may be furnished with a double row of fulcra at the anterior margin of the inferior piece, as I think I have found in *Palæoniscus* and *Acrolepis* (*A. asper*). There are genera of fossil Ganoids the anterior margins of the fins in which are covered with a single row of fulcra as far as the extremity, in which case they are bifid fulcra with simple spiny points. According to Agassiz's description of a row of acute pieces placed along the upper and lower margin of the caudal fins in *Dapedius punctatus* (p. 194), *Dapedius* belongs to this place. I find a single

row of fulcra on the upper and under margin of the caudal fin of *Tetragonolepis* and *Ptycholepis* as far as the extremity. They also appear to be simple in the thoracic fins of this genus, according to Agassiz's plate of *Tetragonolepis confluens* (Ag. ii. tab. 23*a*, fig. 1). *Pholidophorus* also appears to belong to this place, from the fulcra on the upper and lower margin of its tail-fin.

In other genera of Ganoids the anterior margins of the fins are covered with a double row of fulcra, just as we see among living Ganoids in *Lepisosteus*; exactly the same occurs in all the fins of *Lepidotus* and *Caturus*. That the same applies to the thoracic fins of *Lepidotus*, is shown in the figure of *Lepidotus Mantellii*, Ag. (See Agassiz, ii. tab. 30*c*.) I find the double rows in this and in all the other fins, as also on both margins of the caudal fins. In a large species of *Caturus*, from the Lias of Boll, which is probably the *Caturus Meyeri*, V. Münst., I find several strong undivided fulcra at the commencement of the caudal fin; but these immediately pass into double rows of fulcra, which cover the entire length of the anterior margin. I also find these double rows of fulcra on the fins of *Pachycormus macropterus*, Ag., in those parts where fulcra are present, *i. e.* on the dorsal and anal fins. *Semionotus* has also double rows of fulcra (pectoral fins). These differences indicate essential variations; it is impossible to find a more remarkable distinction than the caudal fin of *Ptycholepis* and *Tetragonolepis*, with simple rows of spinous fulcra, and of *Lepidotus* and *Lepisosteus*, with double rows. In *Pachycormus* the double rows occur with an unossified condition of the centre of the spinal column; but in *Lepisosteus*, and apparently also in *Lepidotus*, with an osseous spinal column. According to Agassiz (Ad. tab. 29*c*, fig. 12), the genus has a perfectly ossified spinal column, and thus makes an exception to the other *Lepidoidei*, in which, according to the same author (*l. c.* 182), as far as he is acquainted with the remains of the skeleton, the vertebral column is wanting.

Although the heterocercous Ganoids are much more numerous in the older formations, still all the fish found in them are not heterocercous. It is a very remarkable circumstance, that the forms belonging to the families *Lepidoidei* and *Sauroidei*, Ag., which occur prior to the Jura formation, are heterocercous, as Agassiz has pointed out; but this is rather a consequence of the system than of natural relations; the result is at once destroyed, when we take into consideration *Cœlacanthus* and *Undina*, which

at present are separated from these families. Heterocercy, however, anatomically, insensibly passes into Homocercy. Although many Ganoids which form one limit have no fin-rays above the extremity of the vertebral column, still these occur in the Sturgeons, for before the elongated upper pieces of the tail-fin reach its extremity, inarticulate cylindrical spines, which form the summit of this tail-piece, join on to other unarticulated fin-rays, which are placed upon the chorda, and are of a similar structure to the lower rays of this piece. No sharply-defined character can be drawn from this structure, for as the upper tail-piece becomes successively shortened, it passes into a homocercous tail. The heterocercy of the *Plagiostomi* disappears just as imperceptibly. If we examine a heterocercous Shark, we find beneath the skin, above the vertebral column, just such a beard of a fin, consisting of filiform cartilaginous threads as beneath the vertebral column, only shorter.

In concluding these remarks on the Ganoids, the question occurs as to what subdivisions, sub-classes or orders are to be formed of the other fish.

Cuvier, at the conclusion of the first volume of his *Hist. Nat. des Poissons*, in his remarks on the methodic division of fishes, comes to the conclusion, that the formation of families presented few more difficulties, but that there was still a want of important characters by which to arrange the families satisfactorily into large sections. "But to arrange these genera and families in some order, it would be necessary to take a few important characters whence large divisions would result, which, without disturbing their natural relations, might be sufficiently precise not to allow of there being any doubt as to the place of each fish; and we are not yet in a condition to do this in a sufficiently detailed manner." I think that we have at present arrived at this point of our knowledge, and I will now attempt to develope the great subdivisions of fish according to their internal and external characters, and to limit them by acute definitions.

The section of the Chondropterygii, first instituted by Artedi, confirmed by Gronovius and adopted by Cuvier, appears at first sight to be an unnatural combination of the most varied families; in it we find the Sturgeons, the *Chimæræ*, the *Plagiostomi*, and *Cyclostomi* united. It cannot be doubted that in this section the most perfectly organized fish, which hence approximate to the Reptiles, and the most imperfect, the *Cyclostomi*, as the *Petro-*

myzon and *Myxinoidei*, are combined, whilst the great section of osseous fishes includes those which have proportionately but slight differences.

Pallas and Agassiz have, it is true, separated a portion of these fishes, the Sturgeons, from the others. The former (*Zoograph. Ross. Asiat.*) placed the Sturgeons amongst the fish having opercula and free gills, which he called Branchiata, and opposed to them the order *Spiraculati*, which includes the remaining cartilaginous fishes, our present *Plagiostomi*, *Chimæræ* and *Cyclostomi*. Agassiz, who divides the fishes into four orders, Ctenoidei, Cycloidei, Ganoidei and Placoidei, very properly referred the Sturgeons to the Ganoids; and in like manner he had the Rays, Sharks, *Chimæræ* and *Cyclostomi* remaining, so that his Placoids are the same as the *Spiraculati* of Pallas. Although the Cycloids and Ctenoids cannot be continued as orders, still this division contains new and important elements in the development of the natural system. The Ganoids, in a modified form, remain as a distinct order, and yield a portion of what has hitherto formed their contents to the vertebrate fish. But the *Spiraculati* of Pallas, the *Placoidei* of Agassiz, still combine the most perfect and the most imperfect fishes, which present the greatest differences in their anatomy.

The *Plagiostomi* or *Selachii* of Aristotle, *i. e.* the Sharks and Rays, form an order of fishes which are quite peculiar throughout their entire organization, and differing from all others in their skull, which is undivided, but furnished with jaws; and in the covering of all the cartilages with the above-mentioned characteristic fine mosaic of tessellated pieces of bone, which does not recur throughout the whole system of fishes; in its adherent gills having spiracula in the gill-cavities; in the presence of the gill-arches; the absence of the operculum in the generative organs; for the young males have the peculiar external organs with the accessory testes, whilst in the females the tubes unite above the liver to form a single abdominal orifice; they also have the peculiar glands of the oviduct. The only fishes which are related to them are the *Chimæræ*, which possess a different kind of a finer osseous shell of the cartilages, identity of the intestines, similar structure of the external and internal male organs of generation, accessory testes, the external appendages, the ducts of the ovary, and even the same structure of the tegument of the ovum.

The *Cyclostomi*, on the other hand, merely resemble the *Plagiostomi* in the undivided cephalic cartilage and the spiracula; in all other respects they differ from them, especially in the complete absence of gill-arches; of the jaws; the organs of generation having no oviduct or seminal duct; the complete absence of the muscular tunic; in the arterial trunk or *bulbus aortæ*, and in their two arterial valves.

The Prince of Canino* has correctly conceived the peculiarity of the Rays, Sharks and *Chimæræ*, in forming them into a subclass under the name of Elasmobranchii, whilst he included the *Cyclostomi* as one of his four subclasses under the name of Marsipobranchii. I agree in this arrangement; but the other subclasses, Lophobranchii, the Pomatobranchii (the latter including the orders Sclerodermi, Gymnodontes, Sturiones, Ganoidei, Ctenoidei, Cycloidei), are not confirmed by the present state of our knowledge of the anatomy of the osseous fishes and the Ganoids.

Although I admit the subclass Marsipobranchii or the Cyclostomi, I do not include the *Amphioxus* in it: from the investigations which I have already published, I draw the conclusion, that it cannot be admitted into any known order or subclass of fishes, although it comes nearest to the Cyclostomi in the absence of the jaw and the structure of the skeleton. The grounds which prevent this are the muscularity of the entire vascular system without the presence of a heart, a character not found in other fish, nor even in any other of the vertebrata; the position of the gills in the ventral cavity, with a respiratory abdominal pore; the absence of any distinction between the brain and spinal cord; the reduction of the liver to a blind sac of the intestine, and the ciliary motion diffused over all the mucous membranes. It is the type of a distinct subclass, which I name *Leptocardii*.

Those fishes which have scales, with both lungs and gills and perforated nares, form also a separate subclass, *Dipnoi*, Nob.; *Lepidosiren* belongs to it. The valves are longitudinal and spiral, and are situated in the muscular bulb of the aorta. The intestine has spiral valves, as we find in the *Plagiostomi*, the Ganoids, and some *Cyclostomi*. The oviduct opens into the abdomen; their vertebral column possesses a chorda with apophyses.

* *Selachiorum Tab. Analytica*, 1838.

If we remove these four sections of fishes, two others still remain having opercula and free gills, the Ganoids and the true spinal fishes, which, independently of all other differences, separate at once by their cardiac valves. I call all true vertebrate fishes having two arterial valves *Teleostei*, i. e. perfect osseous fishes. We thus have six subclasses based on solid and certain characters, such as Cuvier desired but failed to obtain.

1. *Teleostei*, Müll. 2. *Dipnoi*, Müll. 3. *Ganoidei*, Agass., Müll. 4. *Elasmobranchii*, Bonap. seu *Selachii*. 5. *Marsipobranchii*, Bonap. or *Cyclostomi*. 6. *Leptocardii*, Müll.

The Ganoids and Selachii I place in the centre; the Ganoids form on the one side the transition to the *Teleostei* and *Dipnoi*, the *Selachii* on the other to the *Cyclostomi* and *Leptocardii*. The *Teleostei*, or true vertebrate fishes, I divide into six orders:—

1. *Acanthopteri*, Müll.
2. *Anacanthini*, Müll.
3. *Pharyngognathi*, Müll.
4. *Physostomi*, Müll.
5. *Plectognathi*, Cuv.
6. *Lophobranchii*, Cuv.

By *Acanthopteri* I mean those only among Cuvier's spiny-finned fish which have double hyoid bones, as I remove the *Labroidei* and those related to them. In the majority the ventral fins are near the pectoral fins. Their swimming-bladder, when present, is always without an air-tube. The families are as follows:—

Percoidei, Cuv., *Cataphracti*, Cuv., *Sparoidei* (including the *Mænides*), *Sciænoidei*, Cuv., *Labyrinthici*, Cuv., *Mugiloidei*, Cuv., *Notacanthini*, Müll. (*Notacanthus*, *Rhynchobdella*, *Mastacemblus*), *Scomberoidei*, Cuv., *Squamipennes*, Cuv., *Tænioidei*, Cuv., *Gobioidei*, Müll. (including the *Cyclopteri*) *, *Blennioidei*, *Pediculati*, Cuv., *Theutyes*, Cuv., *Fistulares*, Cuv.

The family of the *Notacanthini* includes such Acanthopteri, with abdominal or without ventral fins, which have many dorsal spines independently of a dorsal fin, and the clavicle of which, instead of being suspended from the head, is attached to the vertebral column, as in the Eels. The same exists in *Notacanthus* as well as in *Mastacemblus*. It remains to be shown whether *Tetragonurus* belongs to this place.

The *Anacanthini* are fishes which agree in their internal structure with the *Acanthopteri*; their swimming-bladder, when present, has no air-duct, they have also soft rays only. Their

* See the *Abhandlung über die Natürlichen Familien der Fische*, Wiegmann's *Archiv*, ix. 1, p. 295.

ventral fins, when present, are attached to the thorax or throat. Partly Cuvier's Malacopterygii subbrachii and partly Malacopterygii apodes.

Families: *Gadoidei, Ophidini, Pleuronectides.*

The *Pharyngognathi* * comprise the Acanthopterygians and the Malacopterygians, which have the lower hyoid bones united. Their ventral fins are partly situated on the thorax, partly on the abdomen. The swimming-bladder is always closed, and unprovided with an air-tube.

Families: *Labroidei cycloidei,* Müll. *Labroidei ctenoidei,* Müll. *Chromides,* Müll. *Scomberesoces,* Müll.

The *Physostomi* are composed of Malacopterygii; the ventral fins when present are always abdominal: they are the only ones in this subclass the swimming-bladder of which constantly possesses an air-duct. They may be arranged into two suborders, which nearly correspond to Cuvier's Malacopterygii abdominales and Malacopterygii apodes.

To the *Physostomi abdominales* belong the families *Siluroidei,* Cuv. *Cyprinoidei,* Ag. *Characini* †, Müll. *Cyprinodontes,* Ag. *Mormyri,* Cuv. *Esoces,* Müll. *Galaxiæ,* Müll. *Salmones,* Müll ‡. *Scopelini* §, Müll. *Clupeidæ,* Cuv. *Heteropygii* ||, Tellk. (*Amblyopsis.*)

To the *Physostomi apodes* s. *Anguillares* belong the families *Muræenoidei,* Müll. *Symbranchii,* Müll. *Gymnotini,* Mull.

In the family of the *Siluroidei,* Cuv., I separate as groups the true *Siluroidei* or *Siluri,* and the *Goniodontes,* Agass., or *Loricarini.* The family of the *Cyprinodontes,* Ag., or *Pœciliæ,* Val., which I have elsewhere characterised, contains only such fishes as have a protractile mouth, and which is bounded solely by the intermaxillary bone. The genus *Umbra,* Cramer (*Cyprinodon umbra,* Cuv., *Umbra Crameri,* Nob.), does not belong to the Pœcilian genus *Cyprinodon,* Val.: in addition to the intermaxillary teeth, it has teeth in the vomer and palate-bones; the mouth is bounded anteriorly by the intermaxillary bone, externally by the upper jaw, as in *Esox,* with which also it agrees, in the stomach not having any blind sac, and in the intestine and their covered pseudo-branchiæ. *Esox* and *Cyprinodon* are the only two genera now certainly belonging to the *Esoces.*

Through the kindness of M. Valenciennes I have been able

* *Loc. cit.*, p. 305. † Ibid. p. 313. ‡ Ibid. p. 323.
§ Ibid. p. 321. || Mull. *Archiv,* 1844, p. 392.

to continue my examination of the *Esoces*, Cuv. I am uncertain about *Salanx*, as the specimen from the Museum at Paris which I examined was badly preserved and insufficient. The *Microstoma* in the Museum at Paris has the mouth anteriorly bounded by the intermaxillary bones; behind these are the upper jaws, which form the outer portion of the boundary of the mouth. A fat fin, such as is figured in the copper plate of the 'Règne Animal,' is certainly not present in the specimen which has crested pseudo-branchiæ. The *Microstomata* of Risso and Reinhardt belong, on account of their fat fin, to a distinct but nearly-related genus; they agree with one another and with *Argentina* in the teeth not being situated on the intermaxillary bones, but only on the vomer. *Argentina* however has not three, but six gill-rays. The ovary of the *Microstomata* has yet to be examined to ascertain whether they belong to the *Salmones*, and on what grounds. I have also lately examined the *Galaxias* (*Mesites*, Jenyns), which Cuvier also referred to the *Esoces*. The Parisian specimen of *Galaxias alepidotus* has seven gill-rays; another very small species, obtained from M. Poeppig, and probably new, has six gill-rays. The non-protractile mouth of this animal is anteriorly bounded by the intermaxillary bone; behind this we have the upper jaw, just as in *Microstoma*, which bounds the external part of the mouth. I find that the ova of this animal escape into the abdomen, and are expelled through abdominal apertures, as in the *Salmones*, Müll., from which it differs in the structure of the jaw and the absence of the fat fin. *Galaxias* must also be distinguished from the *Esoces*. I provisionally leave them as a separate family, intending to unite them with the *Salmones* when new genera are discovered in this group and render it necessary*. I no longer admit *Clupesoces*, which, in my treatise on the natural families of fish, I separated

* The relation of the ovaries, as to whether the ova escape into the abdominal cavity or are conveyed in an exit-duct of the sacciform ovary, is an important character, subject to no exception. According to Rathke, *Cobitis tænia* is remarkable, from its ova escaping into the abdomen and being discharged by abdominal apertures, which, if true, would form an inexplicable difference from the *Cobites* generally and all other *Cyprinoidea*. According to my observations on *Acanthopsis tænia* and some Indian species of *Acanthopsis*, it is an error founded upon an appearance only. The abdominal cavity lying behind the intestine and ovary is nothing more than the sac of the ovary, which has become adherent to the walls of the abdomen, and to the anterior wall of which behind the intestine the ovarian surface belongs. A comparison with *Cobitis fossilis*, in which the ovarian sacs are double, but have also in their greatest extent become adherent to the abdominal walls, places the matter beyond all doubt.

from the *Clupeæ*. Their difference depended upon the absence of the pseudo-branchiæ in the former. Some species of the genus *Megalops*, obtained from Rich. Schomburgk and Dr. Peters, have convinced me that the pseudo-branchiæ in this genus are evanescently small, and excited a doubt in my mind concerning the *Clupesoces*; I consequently last summer communicated my view to the Prince of Canino, that these families were probably not good. Since that time I obtained *Gnathobolus*, and found that this genus, which is so closely related to *Notopterus*, differs from the former in the possession of pectinated pseudo-branchiæ. It is thus certain that the *Clupesoces* must be given up, that they belong to the *Clupeidæ*, and do not form even a distinct group. To the *Clupeidæ* belong *Clupea*, *Pristigaster*, *Alepocephalus*, *Gnathobolus*, *Notopterus*, *Engraulis*, *Thryssa*, *Amia*, *Megalops*, *Elops*, *Lutodeira*, *Hyodon*, *Butirinus*, *Chirocentrus*, *Stomias*, *Chauliodus*, *Heterotis*, *Arapaima* and *Osteoglossum*. Since the last communication I have examined *Amia* and *Chauliodus* in Paris; neither have pseudo-branchiæ.

The true Eels, with an air-duct to the swimming-bladder, are alone to be referred to the *Anguillares*; whilst *Ophidiæ* are removed to the order *Anacanthini*. But even the *Anguillares* must be separated into the *Murænoidei*, *Symbranchii* and *Gymnotini*. In the former, as we know, the ova and semen pass together into the abdominal cavity, and through abdominal apertures, as in the *Cyclostomi*, and the ova in the *Salmonidæ*. However, I find in the *Symbranchii* (*Symbranchus* and *Monopterus*), and in the *Gymnotini* (*Gymnotus*, *Carapus* and *Sternarchus*), deferent canals and pouched ovaries continuing, as in most osseous fishes, in the oviducts. The families of the Eel-like *Physostomi* may generally be separated readily by the jaws. In the *Murænoidei* the mouth is bounded in its entire length by the intermaxillary bones only, and the upper jaw, which is small from imperfect development, is imbedded in the flesh. These fishes have no cæcum, but a blind sac to the stomach. In the *Symbranchii* (*Monopterus*, *Symbranchus*, *Amphipnous*) the intermaxillary bone also extends to the angle of the mouth, the upper jaw accompanies it to the same spot. Their stomach has no blind sac nor any cæcum. The intestine is quite straight, and is accompanied to its termination by the liver, which is extremely elongated. In the *Gymnotini* (*Gymnotus*, *Carapus*, *Sternarchus*, &c.) the mouth is bounded anteriorly by the inter-

maxillary bone, and laterally by the upper jaw. They have a cæcum, and their anus is situated beneath the throat. The classification of the *Physostomi* now rests on solid foundations; but we must not conceal the fact, that the families of the *Acanthopteri*, in which the characters pointed out by Cuvier are mostly retained, still present many artificial distinctions.

Plectognathi, Cuv.—Although the immoveable articulation of the upper and lower jaws in this order is not constant, and this structure likewise occurs in other fishes, as in several *Characini* (*Serrasalmo*, &c.), still Cuvier's *Plectognathi* have considerable affinity in their cutaneous tegument, the scales, roughness, spines, and (osseous) plates of which differ from ordinary fish-scales. To them belong the families, *Balistini*, *Ostraciones* and *Gymnodontes*.

The *Lophobranchii* form the last order of the *Teleostei*, which do not essentially differ from the vertebrate fish generally.

The *Selachii* form two orders, the *Plagiostomi* and the *Holocephali*. But the *Plagiostomi* must be again divided into suborders, the Sharks and Rays; for the Rays are distinguished from the Sharks by the perfect annular clavicle extending as far as the under surface of the skin of the back; by the gill-cavities being fissured inferiorly; the absence or adhesion of the eyelids; the union of the pectoral fin with the head; by the cartilage of the cranial fins; and what occurs in all the Rays, the coalition of the anterior part of the back-bone to a single large cartilage without any vertebral division, as also occurs in *Pristis*; whilst the Saw-fish among the Sharks (*Pristiophorus*) resemble the Sharks in that as in all other respects. The families of the Sharks are—*Scyllia*, *Nyctitantes*, *Lamnoidei*, *Alopeciæ*, *Cestraciones*, *Rhinodontes*, *Notidani*, *Spinaces*, *Scymnoidei*, and *Squatinæ*. Regarding the families of the Rays, as arranged in the system of the *Plagiostomi*, we need only remark, that the genus *Platyrhina* belongs to the oviparous Rays, hence to the family of the *Raiæ**.

* See *Abhand. d. Akad. d. Wissenschaft* A. D. 1840, p. 246. The relations of the genus *Trygonorhina*, with the ova of which I am unacquainted, are probably the same as those of *Platyrhina*.

Classis, PISCES.

Subclassis 1. Dipnoi.

Ordo I. *Sirenoidei.*

Familia 1. Sirenoidei.

Subclassis 2. Teleostei.

Ordo I. *Acanthopteri.*

Familiæ: 1. Percoidei.
2. Cataphracti.
3. Sparoidei.
4. Sciænoidei.
5. Labyrinthiformes.
6. Mugiloidei.
7. Notacanthini.
8. Scomberoidei.
9. Squamipennes.
10. Tænioidei.
11. Gobioidei.
12. Blennioidei.
13. Pediculati.
14. Theutyes.
15. Fistulares.

Ordo II. *Anacanthini.*

Familiæ: 1. Gadioidei.
2. Ophidini.
3. Pleuronectides.

Ordo III. *Pharyngognathi.*

Subordo 1. Pharyngognathi acanthopterygii.

Familiæ: 1. Labroidei cycloidei.
2. Labroidei ctenoidei.
3. Chromides.

Subordo 2. Pharyngognathi malacopterygii.

Familia 4. Scomberesoces.

Ordo IV. *Physostomi.*

Subordo 1. Physostomi abdominales.

Familiæ: 1. Siluroidei.
2. Cyprinoidei.
3. Characini.
4. Cyprinodontes.
5. Mormyri.
6. Esoces.
7. Galaxiæ.
8. Salmones.
9. Scopelini.
10. Clupeidæ.
11. Heteropygii.

Subordo 2. Physostomi apodes.

Familiæ: 12. Muræenoidei.
13. Gymnotini.
14. Symbranchii.

Ordo V. *Plectognathi.*

Familiæ: 1. Balistini.
2. Ostraciones.
3. Gymnodontes.

Ordo VI. *Lophobranchii.*

Familia 1. Lophobranchii.

Subclassis 3. GANOIDEI.

Ordo I. *Holostei.*

Familiæ: 1. Lepidosteini.
2. Polypterini.

Ordo II. *Chondrostei.*

Familiæ: 1. Acipenserini.
2. Spatulariæ.

Subclassis 4. ELASMOBRANCHII s. SELACHII.

Ordo I. *Plagiostomi.*

Subordo 1. Squalidæ.

Familiæ: 1. Scyllia.

2. Nyctitantes.
3. Lamnoidei.
4. Alopeciæ.
5. Cestraciones.
6. Rhinodontes.
7. Notidani.
8. Spinaces.
9. Scymnoidei.
10. Squatinæ.

Subordo 2. Raiidæ.

Familiæ: 11. Squatinoraiæ.
12. Torpedines.
13. Raiæ.
14. Trygones.
15. Myliobatides.
16. Cephalopteræ.

Ordo II. *Holocephali.*

Familia 1. Chimæræ.

Subclassis 5. MARSIPOBRANCHII s. CYCLOSTOMI.

Ordo I. *Hyperoartii.*

Familia 1. Petromyzonini.

Ordo II. *Hyperotreti.*

Familia 1. Myxinoidei.

Subclassis 6. LEPTOCARDII.

Ordo I. *Amphioxini.*

Familia 1. Amphioxini.

APPENDIX.

I shall add to this treatise some recent *physiological* observations on the *true difference between the bulb of the truncus arteriosus* in the *Plagiostomi* and Ganoids on the one hand, and the osseous fishes on the other. This point is still susceptible of an advantageous physiological development.

In the preceding treatise the muscular dilatation of the *truncus arteriosus* in the *Selachii*, Ganoids, and the osseous fishes, is assumed as of equal importance, and I have confined myself merely to the valvular differences in the interior of this swelling, which is also sufficient in a zoological point of view. However, on a further anatomical and physiological examination of the importance of this swelling, we obtain the unexpected result, that in the osseous fishes it has a remarkably distinct structure, which has not the slightest resemblance to that of the Ganoids and *Selachii*. The fact may be briefly expressed as follows:—The muscular tunic in the arterial trunk of the *Selachii* and Ganoids is a true heart, destined for pulsation like the auricle and ventricle, and also agrees with these in its minute structure. The bulb of the arterial trunk of the osseous fishes however is no segment of the heart, no portion of the active central organ; nor does it pulsate like a heart, but is nothing further than the much-thickened commencement of the artery, in which a peculiar layer of the arteries is swollen to an enormous thickness.

It was generally admitted by anatomists that the muscular substance of the arterial trunk in osseous fishes and *Selachii* was identical. Tiedemann asserts that in cartilaginous and osseous fishes it contracts, and that the contraction followed that of the ventricle. I have myself long considered the above portion as identical in both. But if we reflect on the function and the action of the valves in the one and in the other, we at once begin to doubt. In those fishes in which there are several rows of valves inside the muscular arterial trunk, the muscular tunic of the trunk has evidently the importance of an accessory heart of an elongated ventricle. When it contracts it empties its blood into the true arteries, just as the cardiac bulb of the heart of a frog does. The valves are then separated from the artery by the pressure of the blood; the uppermost extend by their margins as far as the point where the muscular tunic of the artery ceases, above them the artery remains full, but the muscular arterial trunk at the moment of the interval of the cardiac pulsation would be withdrawn from the arteries by the pressure of the blood. In the osseous fishes this is exactly reversed. In them the valves lie between the ventricle and the bulb of the artery. When the ventricle contracts, the bulb and the arteries are dilated. If the bulb could contract in a pulsatile manner, as in frogs, the blood would be forced out of the bulb into the nearest

portion of the artery; but immediately on the contraction of the bulb, the blood would return from the artery, where it is subjected to the pressure of the whole arterial system, and would again fill the bulb as far as the valves in the ventricle; in short, the muscular bulb would here be useless as a pulsatory portion of the heart. After these reflections I was sufficiently interested to observe the heart of the first osseous fish which came in my way whilst in vital activity. I then immediately found that the so-called muscular arterial bulb of the osseous fishes effects no pulsation, and that it differs in this completely from the extremely active *bulbus aortæ* of the Batrachia. On the heart of a *Cyprinus*, *Salmo*, Pike, we observe, that as soon as the pulsation of the ventricle succeeds that of the auricle, the bulb and the arteries continued from it are powerfully dilated by the injected blood; thence, until the next contraction of the ventricle, the bulb and artery again gradually contract, and this contraction occurs in the bulb exactly in the same manner as in the arteries, only more powerfully. It is also impossible by mechanical, electrical or chemical irritation to make the bulb, either when empty or cut into pieces, pulsate or contract.

The next step is to compare the minute structure of the muscular substance of the bulb in the *Plagiostomi* and Ganoids with that of the osseous fishes. We then find that the muscle of the arterial trunk of the *Plagiostomi* and Ganoids consists of transversely striated muscular fibres having the same structure as in the ventricle and auricle. On the other hand, the substance of the bulb in the osseous fishes exhibits no trace of the transversely striated fibres of the heart, but consists of mere bundles of delicate fibres, which have not the most remote resemblance to the former muscular fibres. The substance, in a gradually attenuated form, is continued into a similar tunic of the artery, which is continued over the entire ramification of the gill-artery and again appears in the gill-veins. The bundles of this layer and those of the bulb, may be compared to those which Henle discovered in the arterial tunic, consisting of annular fibres, and in which he placed the seat of organic contraction. The bulb, the walls of which in *Salmo* are about eight times as thick as the walls of the gill-artery, would then constitute a cardiac dilatation of a tonic layer. But our bundles are very elastic; and it is at present problematical whether the bulb possesses organic contractility. In the Sharks, Rays, Sturgeons, or Ganoids,

which have a true prolongation of the heart upon the arterial trunk, the muscular structure which lies external to the artery terminates with a sharp border, and the artery proceeds with its tunics within the muscular ring. On the contrary, the apparent muscle of the bulb of the osseous fishes continues uninterruptedly upwards, merely becoming thinner. The mass of the bulb consists entirely of these gray bundles, which internally form irregular *trabeculæ carneæ*, partly running obliquely, partly longitudinally, but externally they form a very thick transverse layer. The inner layer gradually disappears superiorly, the transverse bundles are perceptible on all parts of the artery as completely coherent layers, and may also be prepared in large fishes, as the Salmon, on which these examinations may be instituted. The gray lamina is internally covered by a thin coat, which mostly consists of undulating zigzag fibres; the thick white elastic layer, which lies externally to the gray layer, is also formed in the same manner. These are the unbranched elastic fibres which I described in the *Vergl. Angiologie der Myxinoiden.* The gray lamina in osseous fishes exists quite separately, and their bundles are not entangled with the white elastic fibres.

The bulb of the osseous fishes can therefore only act like the same layer in the general arterial system, but in a much greater degree. The *Cyclostomi* have not the dilatation of the walls into a bulb. Their difference from the osseous fishes, with which they agree in the position and number of the valves at the arterial mouth of the ventricle, is thus explained. But even in osseous fishes the formation of the bulb varies considerably. I have here merely pointed out the general results of the physiological development of this subject. I shall subsequently treat of it more specially when I have completed various experiments upon the vital properties of the lamina in question, in which I am now engaged, and when a chemical examination of it has been made. We shall thence ascertain whether the substance of the bulbus and its continuation is merely elastic, or if it also possesses a certain amount of organic contractility, which I imagine to be the case, although I have hitherto sought for it in vain. I shall then likewise describe the knotty vascular glomeruli which cover the heart of the Sturgeon, and, connected with the coronary vessels, are imbedded in the lymphatic cavities.

Article XIX.

Further Remarks on the Structure of the Ganoidei.
By J. Müller.

[Read before the Berlin Academy of Sciences on the 12th of March, 1846.]

In my memoir on the structure of the Ganoids, I made known some important internal peculiarities of the Ganoids, and showed that these animals, which resemble the osseous fishes in having an operculum, differ from them in possessing a muscular layer on the arterial trunk and numerous rows of valves within it, as also in possessing a chiasma of the optic nerves, whilst the osseous fishes have only two valves at the arterial orifice of the ventricle and are deficient in the prolongation of the muscular substance of the heart upon the arterial trunk; moreover, their optic nerves proceed simply across one another without intermixing. The Ganoids differ in these particulars from the osseous fishes, but agree perfectly with the *Selachii* (the Sharks, Rays and *Chimæræ*). In addition to these general and absolute internal characters of the Ganoids, I mentioned others, which are also peculiar to them, inasmuch as they are never observed in true osseous fishes, but which do not however occur in all the Ganoids. In these, among other things, I placed the existence of a respiratory opercular gill and the spiral valve in the intestinal canal. The former is present in the Sturgeons, *Scaphirhynchus* and *Lepisosteus*, but is wanting in *Polypterus* and *Spatularia*; the latter is seen in the Sturgeons, *Scaphirhynchus*, *Spatularia* and *Polypterus*, whilst it appears to be wanting in *Lepisosteus*. The absence of the omental fissure in the Ganoids had not then been generally observed. The object of the present communication is to show that the absolute or constant general characters of the Ganoids are more numerous, and that many of those characters which are absent in osseous fishes, but which did not appear to be peculiar to all the Ganoids, are in fact universal.

Since my last treatise, the materials for the anatomy of the Ganoids have considerably increased. Dr. Roemer has sent me a *Spatularia* and a considerable number of specimens of the long-snouted *Lepisosteus*, from North America, in spirit.

The newly obtained *Lepisosteus* has still more numerous valves in the arterial trunk of the heart than the specimen which I examined in Paris; the arrangement of the valves is also different. In the Parisian specimen there were five equally developed longitudinal rows of eight valves, thus in all forty valves. In those recently examined there are eight longitudinal rows of valves; among these four rows are larger, and between them there are four rows of smaller ones. The principal rows contain nine valves, the smaller ones partly less. If all the valves were equally developed there would be seventy-two; however, only from about fifty-four to sixty are developed. This distinction alone indicates a specific difference. The specimens obtained by Dr. Roemer are the ordinary long-snouted species, *Lepisosteus bison*, De Kay, 'Zoology of New York,' pt. 3. Albany, 1842, p. 271, tab. 43. fig. 139. (*Lepisosteus osseus*, Agass. *Poiss. Foss.* ii. 2. p. 2, tab. A. fig. *inf.* and *sup.*) In the Parisian specimen the snout was shorter, as in the Caiman, *Encycl. Méthod.* tab. 71, fig. 292. *Lepisosteus platyrhynchus*, De Kay, p. 273, tab. 43. fig. 137. *L. semiradiatus*, Ag., *Poiss. Foss.* ii. tab. A. fig. ined., which appear to be identical. *Spatularia* has four longitudinal rows of valves, with three in each, within the muscular arterial trunk.

An important new fact in the anatomy of the Ganoids relates to those which have not the opercular gill, *Polypterus* and *Spatularia*.

In those Ganoids which are not furnished with the respiratory opercular gill, the gill-artery still appears necessarily to give a branch to the operculum, so that this artery must be regarded as equivalent to the above gill, or as an aortic arch. I observed this accidentally in *Polypterus bichir*, and it was the same in several specimens. I then found the same branch of the gill-artery going to the operculum in the *Spatularia* sent me by Dr. Roemer*.

* This specimen is one foot and a half long, and has teeth in the upper jaw, palate-bones, lower jaw, and on the anterior part of the two first gill-arches, hence *Polyodon folium*, Lacép., which is however perhaps only *Planirostra edentula* in a young state; for all the specimens hitherto examined which had teeth were young, and those without them were larger. See *Vergl. Anat. der Myxinoid*, i. p. 148. On the summit of the tail there are fulcra, as in the Sturgeons, and the sides of the upper fold of the tail-fin are also furnished with longitudinal osseous plates. The orifice of the pharynx and the posterior and inferior circumference of the gill-cavity are covered with small three-valved cordiform scattered scales. Lacépède was wrong in ascribing five gill-arches

Thus again is manifested the profound obedience to the law which even governs the variations. In osseous fishes the ramification of the gill-artery is always confined to the gills, and it has never been observed to ramify on the operculum. We have, however, a somewhat analogous example in *Lepidosiren*, in which the gill-artery branches to the internal surface of the head. In *Lepidosiren* the appearance is explained by the presence of lungs, which send bright red blood to the heart, so that the arterial trunk conveys mixed blood from the heart both to the gills as also to the body through the above branch and the aortic arches. In *Polypterus* and *Spatularia* the phænomenon may be explained by the absence of the opercular gill.

The diffusion of the gill-artery in a true gill lying anterior to the gill-arches is universal in the Selachii. All the genera of Sharks, Rays and *Chimæræ* which I have examined have an anterior gill (which is quite distinct from a pseudo-branchia) analogous to the opercular gill in the Ganoids, and it is thus proved that the vessels of this anterior gill arising from the gill-artery are present even when the anterior gill has disappeared by retrogressive metamorphosis. I have already pointed out an exactly analogous relation in obedience to the law in the vessels of the pseudo-branchiæ; but it there applies to arteries, which arise from *gill-veins*, not gill-arteries, and which thus carry bright red blood. I may remind the reader of the facts laid down in the Comparative Angiology of the Myxinoids. Thus some sharks have pseudo-branchiæ in the blowing-hole, others have no pseudo-branchiæ, or not even the blowing-holes. The same carotid, which in the former goes through the *rete mirabile* of the pseudo-branchia, becomes lost in it and again formed from it, in *Scymnus* constitutes only a double loop at the blowing-hole, because the pseudo-branchia is wanting, or in the *Carcharias*, which have neither blowing-hole nor pseudo-branchiæ, at that part, where these should be, it forms a plexiform convolution, subsequently proceeding as a simple trunk. Thus the vessels observe the same law when the true as when the false gills disappear; in the former case, from a branch of the gill-artery, which carries dark red blood and is distributed to the opercular gill by the disap-

to *Polyodon*; there are only four. The Sturgeons have had the same fate. Brandt ascribed five gill-arches with gill-plates to them (and moreover, the opercular gill); this error has passed from Brandt and Ratzeburg into Heckel and Fitzinger's Monograph of the Sturgeons. No sturgeon has more than four gills of the gill-arches, and the opercular gill belonging to them.

pearance of the latter, a systemic artery is formed; in the second case, a systemic artery is formed from a branch of the gill-veins carrying bright red blood, *i. e.* from the artery of the pseudobranchia, by the disappearance of the latter. The pseudobranchia, which is wanting in *Scymnus*, I have found in an early fœtal stage*. It may here be asked whether *Polypterus* and *Spatularia* do not, in the fœtal state, possess the opercular gill of *Acipenser*, *Scaphirhynchus* and *Lepisosteus*, which are formed on the general plan of the Ganoids, and if the equivalent which we have found may not be produced by a reduction of the opercular gill? If it be not so, nevertheless enough has been done here on the general plan of the Ganoids in the relation which we have described, and which differs from all the osseous fishes. As the last trace of the opercular gill is preserved in the opercular branch of the gill-artery in *Polypterus* and *Spatularia*, so we find a trace of the blowing-hole in *Lepisosteus*. As such I consider a blind depression in the palate internally to the pseudobranchia; in some individuals it penetrates deeper, and forms a narrow canal, in the same manner as occurs in those sharks which have no open blowing-hole, the *Carcharias*. As this canal is open in the fœtus of *Carcharias*, the same may be imagined to exist in the earliest stages of *Lepisosteus*. The blind canal also exists in the palate of *Scaphirhynchus*. In my previous memoir I was compelled, for want of materials, to leave the relation of the vessels of the opercular gill to those of the pseudobranchia obscure; they are now perfectly cleared up. The former obtains its blood from the gill-artery, the gill-vein of the respiratory opercular gill becomes converted into the artery of the operculum. This proceeds externally to the articulation of the *os hyoides* with the temporal bone, then runs along the inner side of the operculum, and gives off the pseudo-branchial artery. The pseudo-branchial vein becomes the *carotis interna*. It is thus certain that the opercular gill in *Lepisosteus* has a respiratory function, as in the Sturgeons, but that the other accessory gill is either a pseudo-branchia or rete mirabile, and in fact a rete mirabile caroticum, as occurs in the Plagiostomi and Sturgeons, as I have already stated in my first treatise.

Lepisosteus has two carotids, an external and an internal; the internal only of these arteries stands in the relation we have mentioned to the pseudo-branchia as rete mirabile. The carotis

* *Abhandl. d. Akad. d. Wissensch. zu Berlin* for 1840, p. 252.

facialis of *Lepisosteus* arises on each side as a branch of the gill-vein of the first of the four gills, and passes on each side through a separate opening in the great wing of the sphenoid bone into the temporal fossa, to ramify in the external and anterior parts of the head. *Lepisosteus* differs from every other fish in possessing pterygoid processes (formed from the base and ala magna of the sphenoid bone) and the articulation of the pterygoid bones to these processes, of which I know no other example either among the Ganoids or any other fishes. On the inner side of this articulation the pterygoid process is separated from the basilar process of the sphenoid bone by an imperfect canal. The internal carotid coming from the pseudo-branchia entered it inferiorly to turn upwards, and above this fissure the internal carotid immediately enters a foramen leading into the cranial cavity. Hence, on injecting the pseudo-branchial vein with mercury, the vessels within the cranial cavity become filled.

Polypterus has a single internal carotid, which arises from the union of the gill-veins and perforates the centre of the base of the occipital bone in a very peculiar manner.

The arteries of the cellular swimming-bladder of *Lepisosteus* arise from the aorta in great number; the veins empty themselves into the two subvertebral veins. The cellular swimming-bladder is therefore in this instance not of the nature of a lung.

In *Polypterus* the arteries of the swimming-bladders arise from the last gill-vein of each side at about the middle of the gill-arches which have grown to the gill-apertures. The veins of the swimming-bladders proceed to the middle vena cava, which also receives the hepatic veins. This peculiar vena cava impar, which is distinct from the two subvertebral veins, forms a considerable trunk from the posterior extremity of the abdominal cavity anterior to the anus, where it communicates with the subvertebral veins and the caudal vein; at the posterior extremity of the right large swimming-bladder, which extends to the anus, it passes to the posterior extremity of the swimming-bladder anterior to it, and accompanies it, lying between it and the right lobe of the liver, which is very long, as far as the diaphragm. It receives a great number of oblique branches from the right swimming-bladder, and finally, the main venous trunk of the right and left swimming-bladders.

The swimming-bladders in *Polypterus* are completely sur-

rounded by a muscular coat, their mucous membrane merely exhibits very delicate, parallel and minute folds in oblique rows. In *Lepisosteus* the muscular substance forms fleshy bundles lying in the furrows of the cellular divisions; but the arrangement of the small cells is quite independent of trabeculæ carneæ.

All the Ganoids, like the Selachii, possess a thoracic gland. This is the gland which Stenonis first discovered in the Rays (*Anat. Raiæ*), and lies in the centre of the frame-work of the gills, between it and the gill-artery. It was recently described by Simon in the Sturgeons as the thymus gland, and also exists in the same situation in *Polypterus* and *Lepisosteus*; it is usually single, but in *Polypterus* is double; it agrees perfectly in microscopic structure with that of the thymus gland.

The vascular glands on the surface of the heart in the Sturgeons also occur in the *Spatulariæ*.

Agassiz, Valentin and Van der Hoeven, in their descriptions of the intestines of *Lepisosteus*, have not noticed the spiral valve of the alimentary canal. As the intestines had been removed from the specimens which I examined in the Zoological Museum at Paris, and having been placed in the anatomical cabinet were not at hand, I was obliged to leave this point undecided. However, in examining the North American specimens, I find that the spiral valve is always present; it is only rudimentary both as regards its length as well as its height. It is absent in the greater part of the canal, commencing about the extremity just before the large intestine; it makes only three spiral convolutions and is very slightly elevated, so that functionally (increase of surface) it has no action, and is merely an indication of the general plan of organization of the Ganoids. We also thus see that the spiral valve in those fishes which are furnished with it, the Ganoids, Sirenoids and Plagiostomi, begins to be developed at the junction of the chylopoietic canal with the large intestine, and that it increases in length from below upwards, not from above downwards. It attains its maximum of development when, as in the Plagiostomi and in *Polypterus*, it extends as far up as the spot where the bile is poured out, or as far as the duodenal portion of the intestine.

The existence of the spiral valve belongs henceforth to the absolute or general characters of all Ganoids, but nothing of the kind is observed in any of the osseous fishes. Numerous rows of valves in the arterial trunk, a muscular layer on the same, and

a spiral valve in the intestine appear mutually dependent in the Selachii as in the Ganoids. We know of no exception. If we were acquainted with a Ganoid having a spiral valve in the intestine, the arterial trunk and cardiac valves of which had not been examined, we might predict that it would possess a muscular coat upon it and numerous rows of valves within. And, on the other hand, were we acquainted with the latter, but the intestine had not yet been examined, we might predict with equal certainty that the spiral valve would be present. *Lepidosiren* is properly distinguished from the Ganoids.

The sexual organs of the Ganoids are not formed on a common plan; in this point of view there are indeed as well-marked differences among the Ganoids as among the families of the osseous fishes. In the Sturgeons and *Polypterus* the oviducts open into the abdominal cavity, and the ova are conveyed from the abdominal cavity through the infundibulum of the oviduct. *Lepisosteus* has abdominal apertures near the anus. The ovaries are sacciform; the ova are developed in the substance of the internal wall of the sac, which is continued into the oviduct. The oviducts do not proceed from the end but from the middle of the length of the sac, so that the sacs are blind anteriorly and posteriorly. The male generative organs do not present any peculiarities; the seminal duct (vas deferens) in its course presents some vesicular expansions, its ramification in the testes, and the whole testis may be inflated from the vas deferens. The vas deferens leads into the ureter. There is no true urinary bladder, but anterior to the orifice of the urogenital canal there is a considerable sacciform expansion, in which in the females the oviduct also terminates. The urinary bladder is also wanting in *Polypterus*. The reason why there are as great differences in the structure of the sexual organs of the Ganoids as between the families of the osseous fishes, is very interesting as regards the importance and the extent of the section which the Ganoids must form in a system. From this alone it is evident that they constitute far more than a family, and *that their anatomical peculiarities cannot in any case be regarded as characters of a separate family of osseous fishes.* Their location as a sub-class of the same rank as the *Selachii*, *Osteacanthi*, *Cyclostomi* and *Sirenoidei* is thus confirmed, and likewise the difference of family between *Lepisosteus* and *Polypterus* is pointed out anew.

The fissure of the retina of the eye and the falciform process

are absent in *Lepisosteus* as in *Polypterus*, nor is the choroid gland present. The brain had become spoilt.

The ophthalmic nerves are distributed in both fishes as usual to the muscles of the eye, but in their origin *Lepisosteus* presents a very remarkable difference, which I always found the same in several specimens. The trochlear nerve and the motor oculi unite with branches of the trigeminus, *i. e.* are twigs from branches of the trigeminus; at their origin from the brain they are perfectly separable, they then become enclosed in the trigeminus, from which they cannot be separated by dissection. The trigeminus leaves the skull through two foramina, a smaller branch through a distinct aperture in the ala parva, the remaining portion of the trunk through a foramen between the great and small wing. The first branch is then composed of two roots from each trunk. The trochlear nerve and the motor oculi are twigs of that branch of the trigeminus which passes through a separate foramen in the ala parva. The branch for the rectus superior, internus, inferior and the obliquus inferior, contains also the branches for the ciliary nerves. The abducens nerve however passes out with the posterior part of the trunk of the trigeminus through a foramen between the greater and lesser wing of the sphenoid bone.

In *Polypterus* the nerves of the muscles of the eye are all perfectly separate. The trochlear nerve first passes through a distinct foramen, the two other muscular nerves with the first branch of the trigeminus through another foramen. Moreover, a root of the main trunk of the trigeminus which comes out more posteriorly joins the first branch of the trigeminus. The foramen for the trochlearis and that for the first branch of the trigeminus, motor oculi and abducens, are placed in the descending plate of the frontal bone, the foramen for the main trunk of the trigeminus between the frontal and ethmoid bones.

The opercular branch of the trigeminus in *Lepisosteus* and *Polypterus* resembles that in the osseous fishes; in *Lepisosteus* it separates from the trigeminus passing into a canal in the ala magna, perforates the temporal bone, then runs through a tract on the outer side of the preoperculum, and is prolonged on the inner side of the operculum. The accessory gills in *Lepisosteus* receive branches from the glossopharyngeal nerve, which unites in both fishes with the opercular branch of the trigeminus, and is distributed as usual.

The nervus vagus in *Lepisosteus* passes out through a foramen in the lateral occipital bone, in *Polypterus* between the occipital and the mastoid. In *Polypterus* the longer right swimming-bladder receives twigs from the right and left ramus intestinalis, the small left swimming-bladder from the left ramus intestinalis only. *Lepisosteus* has a single lateral nerve, *Polypterus* has two from the vagus—one upper and one lower; the former runs near the upper mesial line beneath the scaly membrane, the lower one proceeds to the lateral line with the lateral lymphatic duct; they both lie above the button-shaped extremity of the rib-like fleshy bundles, which must however be distinguished from the ribs, which are connected with the scales of the lateral line.

Behind the vagus in *Polypterus* two other nerves leave the skull through foramina in the occipital bone, viz. the hypoglossus for the sterno-hyoid muscle and a nerve for the pectoral fin; the latter also receives two spinal nerves. In *Lepisosteus osseus* four other nerves posterior to the vagus pass through the occipital bone; three, the first of which is very delicate, through foramina in the lateral occipital, the fourth through an aperture in the ascending portion of the basilar occipital bone. The two former unite externally with the nervus hypoglossus to supply the sterno-hyoideus. The two posterior ones go to the pectoral fins. Hence it is clearly seen that no value can be placed on the number of the latter cerebral nerves or cranial apertures situated posterior to the vagus; and that a uniform number of cerebral nerves must not be sought for in the Vertebrata. The sympathetic nerve in the Ganoids resembles that of the osseous fishes: in *Polypterus* it runs on each side of the aorta, and is connected with the spinal nerves by very long communicating branches.

We have still to mention a very remarkable appearance in the lower spines (of the caudal portion of the vertebral column) of the Ganoids; in *Polypterus* and *Lepisosteus* they remain as separate bones appended to the vertebral column, exactly as the lower spines of the tail of some mammalia *. The remarkable circumstance is, that these inferior spines in those Ganoids which have an osseous skeleton (*Ganoidei holostei*), do not appear to arise, as in other fishes, from the union of the lower apophyses of the vertebral body (which in fishes in the early state are distinct osseous pieces), but that in *Lepisosteus* they are

* *Vergleich. Osteol. der Myxin.*, 97.

distinctly formed by the union of the ribs themselves. In the osseous fishes it is quite different; in them they always arise, without exception, from the union of the lower apophyses of the vertebral body, *i. e.* of the lower vertebral pieces of the fœtus; and in a great many osseous fishes the ribs are also attached to the lower spines at the extremity of the abdomen. This difference between the *Gonoidei holostei* and the osseous fishes is one of the most important osteological distinctions in the division of the Vertebrata. It is very desirable therefore that we should become acquainted with the fœtal state of the vertebral column in these Ganoids. In the Sturgeons the lower spine arises as usual only from the lower vertebral pieces which cover the whole length of the chord.

Dr. C. Vogt has translated my first treatise on the Structure of the Ganoids and the Natural Arrangement of Fishes into French, in the *Annales des Sciences Naturelles*, 1845, July, and has appended some observations to it; among them there is one which contains a very important fact. In examining the *Amia calva* of the Paris Museum as to the valves and the muscular coat of the arterial trunk, which I instituted as characters of the Ganoids, Vogt has discovered in it a new Ganoid of the present creation. For he found in this freshwater fish from Carolina, which Cuvier placed (together with *Polypterus* and *Lepisosteus*) among the *Clupeidæ*, and which I left there, two oblique rows of valves in the arterial trunk, and in each row five or six valves; moreover, the arterial trunk, as in other Ganoids, was covered externally by a well-defined layer of muscular substance. According to the same observer, *Amia* has a screw-like spiral valve in the intestine, which makes several turns, without however reaching the upper part of the intestine, and which, as in *Lepisosteus*, is confined to that part only of the intestine anterior to the large intestine. Notwithstanding this anatomical resemblance to *Polypterus* and *Lepisosteus*, the scales of *Amia* have not the slightest similarity with the former Ganoids; and we thus again see how little the scales can be trusted. The scales of *Amia* are by no means osseous plates, they are flexible and rounded. Among those fossil fishes which M. Agassiz enumerated as Ganoids, we find similar scales in *Megalurus* and *Leptolepis*, and this is another reason why these two genera, respecting which I have not as yet arrived at any conclusion, from want of positive characters, may possibly be Ganoids. Like

them, *Amia* also resembles in habit the osseous fishes rather than the Ganoids. I had examined its external characters in the specimen at the Zoological Collection in Paris, as also the cellular swimming-bladder among the abdominal viscera in the Anatomical Cabinet of that city*.

Vogt thinks that *Amia* cannot be separated from *Sudis* and *Osteoglossum*, notwithstanding the structure of the arterial trunk, because in other respects they are so similar. According to my observations *Sudis* is an osseous fish, having two valves at the arterial orifice of the ventricle, no muscular covering on the arterial trunk; the same applies to *Osteoglossum*†. This opinion may be so expressed, that these fishes are all either Ganoids or osseous fishes, whether *Sudis* and *Osteoglossum* follow *Amia*, or the latter *Sudis* and *Osteoglossum*. Now Vogt considers *Amia* to be a Ganoid, and therefore *Sudis* would also be a Ganoid. But if we consider *Sudis* as a Ganoid, the anatomical characters would not be exclusive. I can only repeat the principles which I have developed in my previous treatise for separating the false Ganoids. Now, since the anatomical characters of the Ganoids are the only essential ones with which we are acquainted, and which remain constant in them, and as they are exclusive, *Sudis* and *Osteoglossum* are common osseous fishes, for the same reason therefore that many other osseous fishes which were once enumerated among the Ganoids have necessarily been separated. The very object of my investigation was to find out characters and arrange fishes according to their fundamental internal affinities, leaving out all external similarities of form. I think that this proposition is finally solved, and I know of no external characters which would be of sufficient importance to unite two fishes, which are so distinct in their internal structure as a

* In my communication in 1842 and 1843 I passed over *Amia*. It belonged to those fishes which I intended to examine in Paris in the autumn of 1844. There was nothing however in its habit which could excite in my mind the idea of a Ganoid; this was the reason why I did not examine the heart and left it among the *Clupeidæ*. Vogt's observation is so much the more meritorious; undoubtedly his attention was directed to its examination by a recollection of the irregular circular scaled Ganoids of the Old World. I find from my notes on *Amia* that it had no accessory gills, the upper jaw external to the intermaxilla, with an appendix; in the gill-cavity beneath and behind the gills a peculiar long-pointed, flat cartilaginous appendage, covered by a wrinkled membrane, attached to the isthmus and directed towards the shoulder-blade; scales longer than broad; soft, flexible, and striped longitudinally.

† The figure of *Osteoglossum bicirrosum* in *Spix. Misc. Brasil.*, as regards the tail, is either badly drawn, or is taken from a fish with a monstrous tail.

naked and scaly amphibium. As certainly as all naked amphibia agree in having an aortic heart, and all scaly amphibia in not possessing this heart, so do the Ganoids and the Osseous Fishes differ decidedly in this absolute character. The position of *Sudis* and *Osteoglossum* is determined with certainty by their structure, which I have detailed, and equally well is the position of *Amia* as a Ganoid decided by the observation of Vogt.

Hitherto *Esox*, *Belone* and *Lepisosteus* have been considered as so similar and related, that on account of their form they were placed in the same genus. After *Lepisosteus* was separated, the genera *Esox* and *Belone* at least appeared to be inseparable; this affinity has been overthrown by anatomy, so that there can no longer be a question of it*. And in what does the intimate affinity of *Amia* with *Sudis* and *Osteoglossum* now consist? and with *Erythrinus*? which, according to Vogt, may also perhaps be Ganoid, although it is decidedly proved that it belongs to the family of *Characini*.‖ *Amia*, *Sudis* and *Osteoglossum* are fishes with soft fins, abdominal ventral fins, and a hard scaleless head, large cheek-bones, long dorsal and anal fins, and whose upper jaw lies external to the intermaxilla. They agree in these points, which in the present question is not of the slightest importance; innumerable fishes of the most different divisions have a hard scaleless head and large cheek-bones, and it is as little extraordinary in *Sudis* as in *Erythrinus*, *Xiphoramphus* and *Xiphostoma*, and many other *Characini*. The scales of *Sudis* and *Amia* are entirely dissimilar. Those of *Sudis* (*Arapaima*), *Heterotis* and *Osteoglossum* resemble mosaic, granulated on the surface; the scales of *Osteoglossum*, as in other osseous fishes, are concentrically striped; the scales of *Amia* are not compound, and on the surface have engraved lines running parallel to their length.

I still less comprehend why Agassiz, in the third part of his *Poissons Fossiles du vieux grès rouge*, places *Sudis* in the family of the *Cœlacanthi* among the fossil Ganoids. He figures in that work the skeleton of a *Sudis* to illustrate the *Cœlacanthi*. The latter, according to Agassiz, are fishes remarkable in their bones and fin-rays being hollow. In *Cœlacanthus* the ossa interspinosa adhere to the processus spinosi, and the fin-rays do not ramify. All this does not apply to *Sudis*. If *Sudis* were related

* See the *Abhandlung ueber die Naturlichen Familien der Fische*. *Archiv. f. Naturges.*, 1843, i.

to the *Cœlacanthi*, I should consider it as proved that the true osseous fishes of the present world, contrary to all the earlier deductions of Agassiz, extend into the oldest formations of the former world. In his new monograph, Agassiz has *differently* characterized the *Cœlacanthi*, with the addition of some fishes from other families, as Ganoids with round imbricate scales and plaited teeth. These round scales are only distinguished from the scales of the osseous fishes by their enamel. But *Sudis* has neither the enamel of the scales nor the teeth of the *Cœlacanthi*. Accurately speaking, our whole knowledge of these *Cœlacanthi*, which are generally considered as peculiar to the Old World, is uncertain and scanty. The ganoid nature of the true *Cœlacanthi*, in my opinion, depends upon the absence in them of the vertebral body. [*Undina* in Graf. Münster's *Beitr.* v. taf. 2, also examined by me.] On the other hand, we have a decisive knowledge of the nature of *Amia* and *Sudis*, and their organization, which is quite different in the two, can hardly serve to exemplify the doubtful family of *Cœlacanthi*. As I long ago examined *Sudis* anatomically in the specimen in spirit, and the skeleton sent by Rich. Schomburgk, in every respect, I can positively assert that it does not differ in a single point from the general type and plan of all our common osseous fishes of the present world. It approximates moreover by *Osteoglossum* to *Megalops* and *Notopterus*, and by these to *Chatoëssus* and *Clupea*. In my former treatise I have shown that they do not in any instance differ in the pseudo-branchiæ, but form a continuous series.

As *Amia* agrees with the other Ganoids in those relations of its structure which have hitherto been examined, in the muscular covering of the arterial trunk, the numerous rows of valves, and in the spiral valve in the intestine, it may with greater certainty be predicted that it also has a chiasma of the optic nerves, a thymus gland, and an uncleft retina; and as it does not possess any opercular accessory gills, it may be supposed that, like *Polypterus* and *Spatularia*, it has the branch of the gill-artery to the operculum as the equivalent of the opercular gill. Comparative anatomy in its perfect form leads to such necessary consequences, that expressions may be obtained for organizations which resemble the expression of an equation. Only let these expressions be found for any given case, then the unknown quantities may be calculated from those that are known, just as

in an equation. Against the renewed comparison and conjunction of the *Siluroidei*, especially the *Loricariæ* with the Sturgeons and *Scaphirhynchus*, I need not indeed do anything more than refer to generally recognised facts in anatomy; and I shall merely remark that *Scaphirhynchus*, which I examined anatomically, perfectly resembles the Sturgeons, not possessing the slightest similarity to the *Loricariæ*, either in the skeleton or in the intestines; and that even their resemblance in external form is metaphorical, because, on accurately viewing the compared parts, as the mouth or tail, they are completely different. There are as few points of resemblance here as between a pike and a shark. *Loricaria* and *Scaphirhynchus* are as widely separated from one another.

The anatomical characters of the large sections must certainly be absolute, *i. e.* without exception, and they are so, only they have hitherto been too little attended to. How many zoologists and anatomists would have concluded before the present period that all the naked amphibia possess an aortic heart, and that it is absent in all the scaly ones! We know also that an amphibium which possesses an aortic heart undergoes metamorphosis, breathes with gills in the young state, and that an amphibium which undergoes metamorphosis has also an aortic heart. If a reptile has no aortic heart, we at once know that it does not undergo metamorphosis, and *vice versâ*. That in the Ganoids it does not depend upon the rows of valves only is self-evident; the remarkable differences in the valves are here simultaneous with the profound difference in the structure of the heart, and in the existence or the want of perfect septum to the heart. That which obtains among the amphibia, does not necessarily occur among fishes. It is, however, worthy of consideration, that among fishes, those which undergo a remarkable metamorphosis are also furnished with a heart of the arterial trunk. I allude to the Plagiostomi, the fœtal larvæ of which are furnished with external gills. We know as yet nothing of the early state of the Ganoids. Among the Sirenoids, *Protopterus* (*Lepidosiren annectens*) retains the external gills discovered by Peters.

I distinguish absolute from relative anatomical characters. Organs which in certain families, genera or species are wanting, as the swimming-bladder, cannot be made use of in forming the great sections or subclasses, but have a relative value in the subordinate sections; *i. e.* the organ, when present, must be con-

structed according to the principles of the order or family. No value can be attached under any circumstances to the presence of the swimming-bladder, but its structure, when present, is subjected to immutable laws, which we learn as soon as we become acquainted with the true orders and families of fishes. According to this law, among all the *Physostomi abdominales* and *apodes* it is furnished with an air-passage when present, and deprived of the air-passage in all the *Anacanthi* (*subbrachii* and *apodes*), all *Acanthopteri* and all *Pharyngognathi* with prickly or soft fins. According to this law of the relative anatomical characters, the swimming-bladder in the Cyprinoidei and Characini is transversely divided, and when present in the Cyprinoidei, Characini and Siluroidei, is without exception combined with the organ of hearing by a chain of small auditory bones.

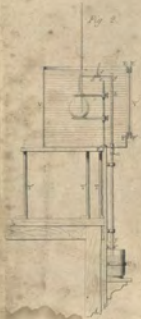
All this led me to an exactly opposite result from that which Vogt deduces from his observations, and with which he concludes his remarks; and I thus prove, that the anatomical characters in a certain sequence of the sections, orders and families are exclusive; that with them alone the classification of fishes can be undertaken; and it may also be expected, that the comparative embryology of fishes, far from yielding facts of a discrepant nature, will confirm that only which comparative anatomy has taught us, as is even now evident as regards the embryology of the osseous fishes and Plagiostomi.

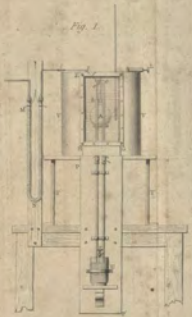
Among the external characters there are some similar to those which we designated as relative anatomical characters, and which belong to the more important—for instance, the fulcra are not peculiar to all the Ganoids, but are absent, without exception, in the osseous fishes. When they occur, they indicate with certainty Ganoids and their complete internal structure; otherwise the external characters are mostly of subordinate importance. No value can ever be placed in the scales, thoracic shield, and such like; they seldom enter into consideration in families, and mostly only in some few genera of families. As the enamel on the scales of the Ganoids is still frequently spoken of, I shall merely observe that *Amia* has no enamel on the scales; the kind of enamel, which consists of elevated lines of a substance different from the body of the scales, occurs in most of the osseous fishes: and, again, osseous fishes occur with dachryoid enamel,

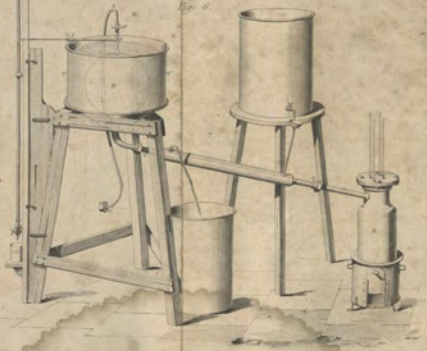
as on the shields of some *Ostracia*. However, I have shown, in my previous treatise, that the *Ostracia* are osseous fishes.

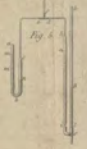
As regards the position of *Amia* in the Ganoid system, it may even now be remarked, that it cannot be referred either to the family of the *Lepidosteini* nor to the *Polypterini*: for it is separated from the former by the absence of fulcra on the fins, from the latter by the absence of that formation of the fin which is peculiar to *Polypterus*—the polyptery of the dorsal fin. I regard *Amia* as the living representative of a peculiar family of Ganoids, genera analogous to which in form, formation of fins, soft scales and osseous vertebral column, may be readily recognised in the fossil *Megalus, Leptolepis, Thrissops* and their allies, in short in the *Ganoidei holostei*, which are unprovided with fulcra to the fins. The difference between the *Amidæ* and the *Cœlacanthi* as families of the Ganoids is sufficiently shown in what has been stated above on the unossified state of the vertebral body in *Undina*; notwithstanding, fulcra have also been observed on the fins of *Macropoma*. The *Lepidosteini* are very numerous in the fossil Ganoids with double rows of fulcra to the fins (*Lepidotus* and its allies): the *Polypterini* have no representatives among fossils.

Finally, it deserves to be considered, what prospect there may be of the number of recent Ganoids being increased by further anatomical examination of the genera as to the characters which I have proposed. Ganoids can hardly be concealed among sea-fishes, and if any should exist, they should be sought for among the few genera of river-fish with abdominal ventral fins which have not yet been examined. North America, and the fauna of Ohio (*Rafinesque ichthyologia Ohiensis*), would deserve especial attention. Among some forms which have not yet been again found, *Sarchirus vittatus* of Rafinesque, I. Acad. Philad. i. 418, tab. xvii. fig. 2, appears worthy of attention, on account of its form. I placed this fish provisionally among the *Scomberesoces*; its position must yet be decided by an examination of the os hyoides and the valves of the heart, &c.









Regnault on the Elastic Forces of Aqueous Vapour.

Article XX.

On the Elastic Forces of Aqueous Vapour.
By M. V. Regnault *.

[From the *Annales de Chimie et de Physique* for July 1844.]

THE theoretical calculation of the work done by steam-engines requires a knowledge of a certain number of laws and physical data which have by no means up to the present time been established with sufficient accuracy. The chief of these data are:—

1st. The elastic forces of aqueous vapour at different temperatures.

2nd. The quantities of heat contained in a given weight of vapour when saturated under different pressures, or, more correctly, the quantities of heat which 1 kilogramme of vapour in a state of saturation under different pressures will give off when it is converted into the state of liquid water at 0° Centig.

3rd. The specific heat of liquid water at various temperatures.

4th. The density which the vapour of water in a state of saturation exhibits under different pressures.

The first of these laws, that which treats of the elastic force of aqueous vapour at various temperatures, is the only one established in an exact manner since the beautiful experiments of MM. Dulong and Arago. The others may be considered as entirely unknown; those which are adopted in practice have been admitted by simple induction, either by extending to vapours those laws which have been observed to apply approximatively to gases, or in slightly modifying those laws according to empirical results deduced from experiments nearly always incomplete and uncertain.

The unquestionable utility attending the completion of our knowledge of the theory of vapours, induced me to undertake the solution of these various questions, well-aware of the great difficulties to be overcome, which however did not appear to me insurmountable. I should have been completely stopped in the execution of this project by the considerable expenses which the procuring and mounting of apparatus would have incurred, had not the Minister of Public Works, at the request of the Central

* Translated by E. Ronalds, Ph.D.

Commission of Steam-Engines, with a liberality that will be appreciated by all friends of science, placed the necessary funds for the execution of the work at my disposal. I propose to publish in a series of memoirs the results at which I shall arrive in these researches, without confining myself each time to any particular order, and reserving for a later period the summary of the whole, when the researches shall have become sufficiently advanced.

In this first memoir I shall treat of the elastic force of aqueous vapour at different temperatures.

The elastic forces of aqueous vapour at different temperatures have occupied the attention of so many natural philosophers, that one would suppose very slight discrepancies must exist in their numerical values. This however is not the case, as may easily be seen by comparing the results which have been published by different experimenters; very great differences are observed, even within the limits of atmospheric temperatures, and it is impossible to decide which of these numbers ought to have the preference. I shall not stop to retrace the history of the researches made upon this subject; the most important are known to all natural philosophers. I pass therefore immediately to the description of my own experiments.

To establish with any degree of precision physical data, it does not suffice that a single mode of experimenting be followed. If the results obtained by one method are not in accordance with the facts which already exist in the science, it becomes often difficult to decide which of these ought to be preferred; for directing our choice in this case we can only be guided by the more or less favourable opinion which we can form of the mode of operating, and the amount of confidence with which the skill of the operator inspires us. It is necessary to repeat the experiments by a variety of methods, and to employ even the modes already adopted by philosophers who have been engaged in the same pursuits, at least when these modes are not absolutely defective. It is necessary to show that all these modes of procedure, when properly carried out, lead to the same result; or if they do not, we must point out by direct experiment the causes of error in the defective methods.

This proceeding is necessarily long and tedious, but it appears to me the only one calculated to introduce certain numerical data into the science, which ulterior experiments can but modify in an insignificant degree. I endeavoured to follow this

method in my experiments on the capacity of bodies for heat, and in those which I made upon the expansion of elastic fluids; it will likewise be adopted in the researches which I now publish on the elastic force of vapours.

I. Nearly all the experiments undertaken for the purpose of determining the elastic force of aqueous vapour at low temperatures, have been made by means of two barometers plunged into the same cup of mercury; into one of these barometers a small quantity of water was introduced, which ascended into the barometric vacuum. The difference in the heights of the two barometers, placed in identical circumstances, represented the tension of the aqueous vapour for that temperature at which it actually was. The great defect of this mode of operating consists in the difficulty of determining exactly the temperature which corresponds to the tension observed. The greater number of experimenters who have followed this method within the limit of atmospheric temperatures, have contented themselves with placing a mercurial thermometer near the barometers, at the same height as the vacuum chamber, and observing the indications; these were presumed to denote the temperatures corresponding to the tension. M. Kaemtz carried out in this manner a long series of observations, extending over the space of two entire years, and he obtained the elastic forces of aqueous vapour from $-19°$ to $+26°$ (*Météorologie*, vol. i. p. 290). The same mode of procedure has been employed by various authors for higher temperatures than those of the atmosphere. In this latter case the two barometers were placed in a glass vessel filled with water, the temperature of which was gradually raised. Dr. Dalton placed only the humid barometer in a second larger glass tube, closed at the base by a cork, through which the barometer-tube passed; he filled the space between the tubes with water raised successively to different temperatures.

This method is not capable of very great accuracy for it is impossible to keep a column of liquid of a certain height at a uniform temperature, without constantly agitating the liquid; and in the experiments of Dalton there exist no means of rendering the temperature stationary for a length of time sufficient to allow of equilibrium of temperature being established between the column of mercury and the surrounding liquid.

I made some experiments in this manner for the purpose of ascertaining within what limits the results were exact.

A dry and a wet barometer were plunged into the same cup of mercury, and both kept in contact with a flat metallic rod, perfectly vertical and divided into centimetres. The cup of mercury was placed in a cast-iron vessel 26 centimetres in diameter, the bottom of which was covered with a layer of mercury to the height of 6 or 7 centimetres, and which could not mix with the mercury in the cup containing the barometers. A tube of glass 23 centimetres in diameter and 1 metre high surrounded the two barometers. This tube was filled with water, which displacing the mercury in the iron vessel, obliged it to rise into the annular space between the exterior of the glass tube and the interior of the iron vessel. A mercurial thermometer dipped into the water of the tube at the height of the barometrical chambers; and lastly, an ascending agitator, furnished with flaps, allowed of motion being communicated to the water in the tube throughout its whole height. The iron vessel was placed upon an iron tripod, under which a furnace could be placed, for the purpose of gently raising the temperature of the water. The tension of the aqueous vapour was denoted in every instance by the difference in the height of the two columns of mercury, a correction being made for the small layer of water in the wet barometer, which covered the top of the mercury.

The water introduced into the barometer should be completely deprived of air. To effect this object, the barometer having been well-boiled, and whilst still hot at the contracted end, I poured out a small quantity of mercury and supplied its place by boiling water which had been kept during half an hour in a state of ebullition. The finger was immediately placed over the opening and the barometer turned round. To be quite certain that the condition was actually fulfilled of introducing water free from air, the barometer was left upright until the following day, then rapidly inclined in order to cause the disappearance of the barometric vacuum: if ever so little air remained in the chamber, a small bubble was observed, which remained for some time, until the water had again dissolved it. It was only after many fruitless trials that I was enabled to obtain moist barometers perfectly free from air.

The difference in height of the two columns was measured by means of a cathetometer; the use of this instrument may give rise to considerable errors, if an endeavour is not made to correct the deviations which the rays of light are subjected to

by refraction, in consequence of the unevenness of the blown tube of glass. It was for the purpose of discovering these deviations, and correcting them when necessary, that the two barometers were adapted to a long vertical metallic scale divided into centimetres. The distances between these divisions were read off with the cathetometer, before the tube of glass was interposed; the same was done when the tube was placed round the barometers and filled with water, and it was observed whether the distances remained the same. In those cases where the distances were but slightly different, it was easy to keep account of the displacement, and to make the correction for the observed height. The tube forming part of my apparatus presented very great irregularities of this kind, so that I judged it prudent not to use it: the corrections which must have been made for the heights observed were frequently considerable, and gave rise on that account to a still greater uncertainty.

I replaced the tube of glass by one of iron plate of the same diameter, cylindrical at the bottom, and terminated at the top by a square case, two opposite sides of which were formed of flat glass, chosen for the purpose. The divisions traced upon the scale then retained the same distances when viewed directly, or through the water of the tube.

For raising the temperature, a furnace is placed under the iron vessel, and from time to time the water agitated in the tube; when the temperature approaches that point at which the observation is to be made, the greater part of the charcoal is removed, and the water is continually agitated in the tube, until the thermometer placed at the height of the barometric chambers ceases to rise; a considerable time elapses before this takes place, and the difference of height in the two columns is measured at the moment of its maximum. In order to make a second experiment, the glowing charcoal is again placed in the furnace and the ascent of the thermometer again determined; when this is effected the charcoal is removed, and the operation repeated as before. Thus two determinations at very nearly the same temperature are obtained.

This method gives very accurate results for temperatures that are the same or a little higher than the surrounding temperature; but it ceases to do so at temperatures a little more elevated. The water then separates so easily into layers having different temperatures, that a uniform temperature can only be

maintained by a constant and rapid agitation: as soon as this ceases, to allow the observer time to measure the difference of level in the two mercurial columns, the separation into layers immediately begins and the determinations become inaccurate. I made, by means of this method, a pretty large number of determinations of the elastic force of aqueous vapour between +10 and +30 degrees; temperatures which differed but little in each case from the surrounding temperature. I shall not however enumerate them here, as they are identical with those which I shall give presently, and which were made with apparatus that I consider more appropriate. Another series of experiments was made with an apparatus consisting of two barometers, the one dry and the other wet, without heating the mercurial columns throughout their whole extent.

Two barometers as nearly alike as possible, having 14 millimetres interior diameter, are placed side by side on a board P P′ Plate VII., fig. 1. These barometers are passed through two round holes *a b* in a case of galvanized sheet-iron V V′ V″, and fixed in these holes by means of caoutchouc. The case, of which a horizontal section is given at fig. 3, has at one of its sides a rectangular opening E F G H, round which is fixed a frame of iron. A plate of glass with parallel surfaces is fitted to this frame by means of a second iron frame E′ F′ G′ H′, similar to the first, and the two are fastened together by screws. A thin strip of sheet caoutchouc cut into the shape of these frames is placed between the glass and the frame E F G H, thus rendering the fastening hermetical. This arrangement allows of the glass being removed and replaced with the greatest ease. The two barometers dip into the same cup U. The iron case has a capacity of about 45 litres; it is placed upon an iron support T T′ T″.

To ascertain whether the interposition of the glass and the water which filled the case produced a deviation in the luminous rays, capable of causing an error in reading off the levels by means of the cathetometer, a fine horizontal scratch was made previously upon the dry barometer at about the ordinary height of the mercury, and centimetre divisions were traced upon the wet barometer. The distances from the marked point upon the dry barometer to all the consecutive divisions upon the wet barometer were then read off,—1st, when the glass was not interposed; and 2ndly, when the glass was in its place, and the vessel

filled with water. The interposition of the glass plate and water was thus observed to produce an absolute deviation in the rays of light, which sometimes amounted to half a millimetre; but the relative deviations in the divisions traced upon the wet barometer in respect to the marked point upon the dry barometer, were always much smaller; these deviations, which are the only ones that could affect the observations, never exceeded 0·10 millimetre; they were nearly always still smaller, and often too small to be worthy of notice. At the same time great care was observed in placing the barometers quite vertical and parallel to the glass plate.

The case V V′ V″ is filled with water, which is kept constantly agitated; a very delicate mercurial thermometer dips into the water, and is observed by means of a small telescope, L, placed horizontally.

The observer directs the telescope of the cathetometer to the top of the mercurial meniscus in the wet barometer; at the moment of observation the motion of the water is stopped, and immediately recontinued, after reading off the height of the first meniscus. Then it is again stopped for a moment, to allow the observer to read off the meniscus of the dry barometer. The water is thus kept in continual agitation, facilitated by the large capacity of the vessel.

The observations can be made with great precision at the temperature of the surrounding air, and can be repeated as many times as is wished. To determine the elastic force of vapour at more elevated temperatures, a portion of the cold water is drawn off by means of a siphon, and replaced by hot water; below the bottom of the iron vessel a spirit-lamp is placed, which can be brought as near as convenient to the bottom, or by regulating the height of the wick, can be so managed as, with constant agitation of the water, to secure a perfectly stationary temperature throughout. This condition is easily attained after some trials, and when the temperature of the water does not exceed 50° C., it is easy to retain it at a stationary temperature for any length of time; the only requisite is, that it be agitated rapidly and continually.

Three or four observations are made at the same temperature thus kept stationary, and between each two consecutive observations an interval of eight or ten minutes is allowed to elapse. Sometimes the temperature of the bath is purposely made to rise two or three hundredths of a degree during the interval be-

tween two observations, or it is allowed to get lower, and then again made stationary by regulating the lamp. It was thus easy to observe that the movements of the mercurial column followed the slightest changes in the thermometer, and precisely the same tensions were observed when the thermometer indicated the same temperature.

By this mode of experimenting, the columns of mercury in the two barometers are not heated throughout their whole height, but those portions which rise above the vessel are subject to exactly the same conditions. The difference in the height of the two columns is taken at the temperature of the bath; this difference, brought down to zero, gives the tension of the aqueous vapour.

The question might still be raised, whether the whole of the chamber filled by the vapour has exactly the same temperature as the bath; whether the surface of the mercury, for instance, has not a lower temperature, in consequence of its connexion with the mercury below, which is colder. This last circumstance certainly takes place, if the level of the mercury is allowed to sink nearly to the bottom of the vessel; but in my experiments the level always remained several decimetres above the bottom. It appeared however desirable to assure myself of this circumstance by direct experiment. I fixed in the circular holes of my sheet-iron vessel two tubes, 14 millimetres in internal diameter, and closed at bottom; the open extremity of these tubes extended above the level of the water in the vessel, and their closed extremities were fixed at the height of the level of the mercury in the cup U. One of these tubes contained mercury which ascended to the same height as the level of the mercury in the real barometer, the place of which it occupied. The mercury in the second tube only rose to the lowest point that had been observed in the wet mercurial barometer during the experiments on the elastic force of aqueous vapour. The vessel V V′ having been filled with water at the surrounding temperature, after the expiration of some hours the difference of level was observed by the cathetometer; then the temperature was raised successively up to 50°, and from time to time the difference of level in the columns, after having rendered the temperature stationary, was read off, as in the actual experiments on the tension of vapour.

The differences observed in the level under these different conditions, reduced by calculation to 0°, ought to remain con-

stant, if the two columns are equally influenced by the corresponding parts. This, in fact, was found to be the case, no difference having been observed which exceeded 0·07 millimetre.

The water in the vessel being kept stationary at a temperature of 45° by means of the lamp, the reservoir of a very delicate thermometer was immersed in the mercury of the tube which contained this liquid at the lowest level. After the lapse of two or three minutes, it indicated an absolutely stationary temperature, it was then quickly taken from the tube and plunged into the water of the vessel; not the least elevation of temperature was perceptible, though the thermometer was capable of showing with accuracy about the $\frac{1}{50}$th of a degree. A second thermometer immersed constantly in the water of the vessel proved, besides, that the temperature of the water had not changed during the interval employed in reading the indications of the first thermometer.

The surface of the mercury in the wet barometer was covered by a layer of liquid 3 or 4 millimetres in height; this layer, by its weight, would depress the level of the mercury, but, on the other hand, it would tend to heighten it by its capillary action. By measuring with the cathetometer the distance between the lowest point of the concave meniscus formed by the water and the summit of the convex meniscus of the mercury, and dividing this distance by 13·5, the density of mercury compared with water, we obtain the little height of mercury equivalent to the column of water thus estimated. The capillary action of the water was determined by direct experiment. To the upper extremities of the two barometric tubes, used in the preceding experiments, two tubes of small calibre, previously cemented into a copper tube having three arms, were joined. The third arm was furnished with a glass tube communicating with the air-pump. Between one of the barometric tubes and the copper tube was placed a U-shaped tube containing pumice-stone moistened with sulphuric acid. The two barometers dipped into the same cup of mercury. A vacuum was produced several times with the air-pump, and the air admitted to dry the sides of the tube in connexion with the sulphuric acid. Lastly, a vacuum was again made, and the tube communicating with the air-pump sealed by fusion; the level of the two columns being then the same, a small quantity of water, about as much as was used in the experiments upon vapour, was passed up into one of the tubes. There were now two imperfect barometers communicating with

each other, subjected internally to the same pressure; the one however was dry, the other, on the contrary, contained a small layer of water. They were left till the following day, to make sure of their being at the same temperature; when the difference of level in the two mercurial menisci and the height of the column of water was determined. This last height, reduced to its equivalent in mercury, would represent the observed difference in the two columns of mercury, if no alteration had taken place by capillary action. The effect of this latter cause would therefore be measured by the difference of height in the two mercurial menisci, less the value in mercury of the little column of water. It was thus found that the wet column, after the correction had been made for the weight of the small column of water, was raised by the capillary action of the water 0·12 millimetre.

Table I. shows the results obtained by this mode of proceeding.

TABLE I.

Temperatures. Thermom. No. 7.	Tensions of the vapour.		Difference.	Temperatures. Thermom. No. 7.	Tensions of the vapour.		Difference.
	Observed.	Calculated.			Observed.	Calculated.	
°	mm	mm	mm	°	mm	mm	mm
9·73	9·03	9·002	+0·03	38·09	49·55	49·543	+0·01
9·73	9·05	..	..	40·28	55·73	55·733	0·00
11·64	10·27	..	..	40·28	55·67	..	..
11·62	10·19	10·200	−0·01	40·25	55·55	..	..
11·62	10·23	..	..	46·20	75·76	..	..
13·56	11·62	11·575	+0·05	46·24	75·96	..	..
13·56	11·60	..	..	46·23	75·88	76·04	−0·16
15·56	13·18	13·16	+0·02	51·39	98·29	..	..
15·58	13·16	..	..	51·39	98·23	98·541	−0·31
17·67	15·07	..	..	58·62	139·05	..	..
17·68	15·13	..	..	58·56	138·81	139·119	−0·31
17·68	15·05	15·052	0·00	58·49	138·25	..	..
19·36	16·74	16·716	+0·02	21·08	18·66	..	..
19·35	16·70	..	..	21·08	18·64	18·585	+0·06
21·41	18·94	..	..	21·08	18·62	..	..
21·41	18·96	18·965	0·00	8·79	8·44	..	..
21·41	19·00	..	..	8·79	8·44	8·454	−0·01
23·66	21·74	21·736	0·00	8·79	8·46	..	..
23·67	21·78	..	..	4·32	6·32	..	..
23·66	21·76	..	..	4·33	6·30	6·239	+0·06
26·01	25·05	..	..	4·34	6·28	..	..
26·02	25·07	25·059	+0·01	4·94	6·54	..	..
26·02	25·07	..	..	4·97	6·54	..	..
28·80	29·44	29·437	0·00	5·00	6·56	6·534	+0·03
28·80	29·46	..	..	6·15	7·06	..	..
31·95	35·27	35·259	+0·01	6·17	7·10	7·081	+0·02
31·95	35·29	..	..	6·19	7·12	..	..
34·79	41·29	..	..	6·22	7·14	..	..
34·75	41·25	41·252	0·00	7·50	7·73	7·745	−0·01
34·75	41·23	..	..	7·51	7·69	..	..
38·09	49·51	..	..	7·52	7·71	..	..
38·09	49·59	..	..				

II. The second series of experiments was made by means of the apparatus represented at figs. 1, 2, 3. A globe A, containing about 500 cubic centimetres, encloses a small glass bulb entirely filled with water recently boiled. The globe is attached to a bent tube, which is cemented into a copper connecting piece having three arms, *d e f*. In the arm *e* a bent tube *e g h* is cemented, and this is fused into the upper part of a barometric tube *h a*, which passes through the opening *a* in the sheet-iron vessel V V′. Through the second opening *b* in the sheet-iron vessel a real barometer is passed, which dips into the same cup of mercury, U. To the third arm of the copper connecting piece is attached a tube communicating with the air-pump, but between it and the pump is interposed a tube M N filled with fragments of pumice-stone moistened with sulphuric acid, of about one metre entire length.

The apparatus being thus arranged, a vacuum is produced a great many times, and after each time the air is admitted very slowly through the tube M N, which dries it as it passes. Having repeated this forty or fifty times, the globe and barometric tube may be considered quite dry; then a vacuum is made for the last time, and rendered as perfect as possible. The air-pump at my disposal could only be made with much difficulty, in the first experiments, to give a vacuum within 2 millimetres; but having been cleaned, the vacuum was often obtained within less than 1 millimetre.

When the vacuum is as perfect as possible, the tube *f l* is sealed by means of the lamp. The globe A is surrounded with melting ice, and after some time the difference in the height of the two columns of mercury is taken with the cathetometer; thus the elastic force of the dry air remaining in the globe at 0° is obtained. The ice is then removed: the globe is heated by a few pieces of charcoal placed in a ladle with a bent handle, and the bulb is broken by the expansion of the liquid contained in it; the globe is again surrounded with melting ice, and after some time the difference in the height of the two menisci is observed. This difference, less that which existed between the heights of the two menisci before the fracture of the bulb, gives the elastic force of aqueous vapour for 0°. Care is taken to repeat these measurements a sufficient number of times, at intervals of about ten minutes, in order to be sure that the differences of height are quite constant.

For making observations at higher temperatures, the glass is fitted into its frame E F G H, the vessel is filled with very clear water, and the operation conducted in precisely the same manner as in the first series, page 565. In order to estimate the prismatic deviations of the rays of light produced by the interposition of the water and the glass, care must be taken, as in the first series of experiments at page 564, to make a mark upon the tube *b o*, and to divide the tube *a h* into centimetres. By this method the results recorded in Table II., Series A, B, C, were obtained.

It is of importance that in all the experiments the barometer should be perfectly correct, and that the apparatus be so arranged as to allow of comparison being easily made between the barometer *b o* and a standard barometer, at any moment during the experiments. For this purpose, the board on which the barometric tubes are fixed has attached to it a piece of metal *r* in which moves a vertical screw *v*, terminated at both extremities by rounded points. This screw is turned until its lower extremity is exactly at the level of the mercury in the cup. The glass is not placed in its frame, and the distance from the level of the mercury in the barometer *o b* to the upper point of the screw is measured with the cathetometer. To obtain the exact height of the barometric column, it is only necessary to add to this distance the length of the screw between its two points, which can easily be done with the same cathetometer, by raising the screw to a convenient position.

The delicacy of the barometer can likewise be tested in another manner, which is equally susceptible of great exactitude. By pouring a larger quantity of mercury into the cup U, or by lessening the quantity of that liquid, the capacity of the barometric chamber can be made to vary considerably; if the barometer is perfectly free from air its height ought to be the same, whatever may be the capacity of the barometric vacuum; it is however no longer the same when the barometer contains the least trace of air*.

The same apparatus is very convenient for determining the elastic forces of aqueous vapour at low temperatures; only in this case, I do not use the sheet-iron vessel V V′ V″, but in its

* This last mode of verification has long since been shown by M. Arago, who made use of the same principle in constructing barometers that a traveller could fill upon the spot without having occasion to boil the mercury.

stead a bell-glass of smaller dimensions, containing about 20 litres of fluid. The barometric tubes are then simply attached to their board, and the globe A is placed at a greater distance from the tubes. The globe is first surrounded with melting ice to determine the tension of the vapour at 0°; the ice is then removed, and into the bell-glass a concentrated solution of chloride of calcium is poured, the temperature of which is constantly lowered by dissolving ice in it. This mixture ought to be constantly stirred, and we obtain easily, not a positively steady temperature, but one at least which oscillates within very narrow limits, for as long a time as is required, by adding small quantities of broken ice as often as the temperature begins to rise. For obtaining the greatest degrees of cold, crystallized chloride of calcium was used, in alternate layers with snow. This mixture was constantly stirred until it became fluid; the temperature was thus gradually lowered until there remained but a very small quantity of ice swimming on the top of the liquid. The observation was made at the moment of minimum temperature, the liquid being rapidly stirred; this minimum could moreover be retained for some time, by adding small quantities of snow.

For elevating the temperature of the bath, small quantities of a hot saturated solution of chloride of calcium are poured into the bell-glass, until a sufficient elevation of temperature is produced. A hot solution of chloride of calcium is used in preference to pure water, that the frigorific power of the liquid composing the bath may not be diminished, and that we may again be enabled to lower the temperature by the addition of powdered ice.

It is evident that the temperature will be rendered stationary so much the more easily as it approaches that of the surrounding air, and it is in this case that the variations in the elastic force of aqueous vapour with the temperature are the most sensible. Below −20° a change of some tenths of a degree in the temperature produced no sensible variations in the elastic force of aqueous vapour. The experiments made in this manner are noted in Table III., Series F, G, H.

The mode of procedure, modified in the manner I have just described, may serve for inferior temperatures to those of the surrounding air; but I have satisfied myself by direct experiment that it likewise affords accurate results for temperatures

higher by many degrees than those of the air. For this purpose the globe is again placed in the sheet-iron vessel V V′ V″, which can be easily done without displacing anything; the barometric tubes remain outside the case, and the openings *a* and *b* in the sheet-iron vessel are closed by corks. The observations are sufficiently accurate when the water is not raised more than from 10° to 15° above the temperature of the surrounding air, but beyond that limit the water of the globe begins to distil and condense in the tubes, and the observations become no longer exact. The series D, E were obtained in this manner.

The methods which I have been describing are capable of great exactness; the apparatus is easily arranged, and is equally applicable to the determination of the elastic forces of vapours which exist in air more or less rarefied. It is sufficient for this latter purpose, to replace the two barometers by a system of two tubes communicating with each other, as is represented in Pl. VII. at fig. 8. In this manner I determined the elastic force of the vapour of water in air, at the ordinary pressure, in order to ascertain whether this elastic force was really the same as *in vacuo*; but I shall reserve this for future publication.

It is essential to the accuracy of the experiments, that the globe be most completely dried before the bulb is broken; this point is attained by producing a vacuum a great number of times with a good air-pump, and allowing, after each time, dry air to enter. I wished to satisfy myself whether it was not possible to dry the apparatus still more perfectly by heating the globe to a high temperature whilst the air was being pumped out, and by this means to obtain higher values for the tensions of vapour at 0°.

The apparatus was modified in the following manner:—the glass bulb containing water was not placed in the globe, but in a small lateral tube *m n*, fig. 4, which is cemented on one side into the copper tube *f*, and communicates on the other with the tube containing the sulphuric acid and pumice-stone. The apparatus is dried in the ordinary manner by the air-pump; but in order to render the drying more efficacious, the globe is surrounded with charcoal and heated to 300° or 400°; the barometric tube is at the same time slightly heated. The air-pump exhausts the air at last in a more complete manner than when the globe is not heated. The tube *l* is closed by the lamp. That equilibrium of temperature may be established in the baro-

metric tubes, the whole is left until the following day; the globe is then surrounded with ice, and the elastic force of the air remaining in the apparatus is determined at 0°. Without removing the ice which surrounds the globe, the bulb enclosed in the tube *m n* is broken by expansion, and the water distils into the globe; the tube *m n* is detached by fusing the capillary portion at *k* with the lamp. The apparatus is now arranged, the experiments are made in the same manner as before; in this manner the results I, J, K of Table III. were obtained, which show the elastic force of aqueous vapour at 0° to be somewhat less than was obtained by the first mode of procedure.

It is easy, lastly, to make use of the apparatus at figs. 1 and 2 for determining the tension of aqueous vapour in an absolute vacuum. For this purpose the water is not enclosed in a bulb, but a certain quantity is placed at once in the globe. When the apparatus is arranged in the ordinary manner, a vacuum is produced by the air-pump, and the globe A is heated with some charcoal, in order to distil over the small quantity of water which has condensed in the barometric tube *a h*. On continuing the action of the air-pump, a constant distillation of the water in the globe and of that in the barometric tube is produced; this water condenses in the tube M N containing the pumice-stone moistened with sulphuric acid. Having distilled in this manner a few grammes of water under very low pressure, it may be presumed that the air has been completely expelled from the apparatus, the tube *l* is then sealed by the lamp. The determination of the elastic force of the vapour is then made in the usual manner.

The series L, M of Table III. were obtained in this manner.

III. The modes of procedure which I have just described are alike applicable to the determination of the tension of vapours produced from other liquids besides water, and require but a very small quantity of material. When these liquids are of a nature to attack the cement, the tubes must be cemented on to the exterior of the connecting piece *e d f*; it is also convenient to use tubes ground with emery to fit the copper connecting piece as nearly as possible. The apparatus represented at figs. 1 and 2 is however only applicable to the determination of elastic forces below 200 millimetres. When it is required to determine more considerable tensions, I employ the apparatus represented at fig. 5. This apparatus I never used for the vapour

of water, but I made use of it frequently to determine the elastic forces of very volatile liquids, as æther, sulphuret of carbon, &c., which will be published in a future memoir.

It is composed of a bent tube *a b c*, 15 millimetres internal diameter, and terminated by a narrower bent tube *c e*. The closed arm *a b* is filled with mercury, which is carefully made to boil, to free it completely from air and moisture. When the mercury has cooled, a small quantity of the volatile liquid is introduced into the branch *b c*, and made to boil for a few moments to expel any air which it might hold in solution; the tube is then inclined in such a manner as to allow a small portion of the hot liquid to pass into the closed arm *a b*. The portion of liquid remaining in *b c* is then expelled by boiling; to effect this more completely, an imperfect vacuum is made by a small pump, if it can be easily managed. The arm *b c* thus remains filled with dry air.

The tube *a b c* is then fixed into the sheet-iron vessel V V′ in a perfectly vertical position opposite the glass. The tube *c e* is cemented into a connecting piece of copper with three arms *e d f*, the arm *d* of which communicates with the manometrical apparatus *h i l k*, furnished with a stop-cock *r*. To the arm *f* is cemented a narrow tube *f g*, which in case of need can be brought into connection with a small air-pump. The two connected tubes *i h*, *k l* are completely filled with mercury; the air contained in the apparatus escapes by the open tube *f g*: this tube is then closed by the lamp. In order to diminish the pressure, mercury is allowed to flow out of the manometer by opening the stop-cock *r*; the air enclosed in the arm *b c* expands into a larger space, and its elastic force diminishes. The mercury is allowed to escape until the level in the closed arm *a b* descends to *m*. The tension of the vapour is then measured by the pressure of the atmosphere, less the column of mercury $\alpha\beta$ in the manometer and the column *m n* in the bent tube *a b c*. The capillary influence of the small layer of liquid above the meniscus in the tube *a b*, is determined, at the close of the experiments, by direct measurement, after equality of pressure has been established in the arms *a b* and *b c* by opening the tube at *a*.

The vessel V V′ is filled with water, maintained at a constant temperature in the manner described at page 565.

It is easily ascertained, by the following method, whether the apparatus is properly arranged, and whether the arm *a b* is com-

pletely freed from air. A first series of experiments is made with the level of the mercury at *m*; this level is then lowered to *m'*, by allowing more mercury to flow out; the space occupied by the vapour is now double what it was in the first experiments; if the least quantity of air was contained in the arm *a b*, the tension of vapour found by the second experiments would no longer be the same as that found by the first.

If it is required to determine by the same proceeding the tensions of a slightly volatile liquid at low temperatures, the tube *f g* is placed in communication with a small air-pump, by means of which the air enclosed in the arm *b c* is previously rarefied, and then the tube *f g* is sealed with the lamp. The arrangement of the handle of the stop-cock *r*, penetrated by three holes, fig. 5 *bis*, renders these different manipulations very easy.

When experiments are to be made at higher pressures than those of the atmosphere, the tube *f g* is sealed at the moment when the manometer contains no mercury. Mercury is then poured into the tube *k l*, the air enclosed in the tube *h i* is thus forced into less and less space, and increases in elastic force.

The method which I have just described is exceedingly convenient for very volatile liquids, because it allows of the determination of their elastic forces between very extended limits. I did not employ it for water, because I consider it, on account of the number of measurements it requires, much less exact for weak tensions than the methods I have previously described, in which I endeavoured to diminish the number of measurements as much as possible *.

The menisci in the bent tube *a b c*, and in the manometer

* This method is similar to that recently employed by M. Magnus for determining the elastic force of aqueous vapour between 0° and 100°, in a memoir which has just appeared (Poggendorff's *Annalen*, lxi. 226). [A translation of the memoir here referred to will be found at page 218 of the present volume of the Scientific Memoirs.] It differs in the mode of obtaining the constant temperatures at which the observations ought to be made. M. Magnus employs for that purpose an apparatus composed of several concentric cases of sheet-iron, which are heated from below by means of spirit-lamps. I had occasion in a note inserted in *Annales de Chimie et de Physique*, tome vi. p. 370, to offer some objections to that method. M. Magnus thinks to have refuted my objections, by describing an experiment in which two air-thermometers, placed in such a manner that one instrument completely surrounded the other, rose exactly in the same ratio when the temperature was raised gradually to 250°. I do not think that that experiment removes the difficulty; I cannot conceive, in fact, how two air-thermometers could show any sensible difference when placed under the circumstances described by M. Magnus.

h i l k, were read off simultaneously by means of two cathetometers and two observers. This precaution is essential, particularly when the tensions are rather considerable, because the air contained in the tube *h i* of the manometer acts as an air-thermometer; if the observations were made successively, notable errors might arise from the displacement of the menisci produced by slight changes of temperature occurring in the surrounding air.

In the greater number of the foregoing experiments, the column of mercury which serves to measure the pressure is heated to the same temperature as the vapour of which the tension is to be measured, and sometimes the space in which the vapour is eliminated is in easy communication with the tube containing the mercury; that is especially the case with the apparatus described at page 563. Now, if within the limits of temperature at which we are operating, the tension of the vapour of mercury is a notable quantity, this tension will be added to that of the liquid under examination and render the determinations inexact. It therefore becomes necessary to determine in a direct manner the elastic force of mercurial vapour between 0° and 100°. I have shown at page 572 that sufficiently exact values could be obtained for the tension of aqueous vapour, even when the barometric tube which measures the pressure is at a temperature 8° or 10° below that of the globe in which the vapour is formed. I have had occasion to prove the same fact with essence of turpentine, even for still greater excesses of temperature. It is probable, that in this case, it is the air remaining in the apparatus which, pressed back into the barometric space, transmits the pressure exhibited in the globe.

I thought that this method would be still more applicable to the determination of the elastic force of mercurial vapour between those limits of temperature at which it is extremely weak. I introduced into the globe of the apparatus, figs. 1 and 2, with the barometric tubes outside the vessel V V′, about 300 grammes of very pure mercury, and produced a vacuum a great number of times, warming the mercury to dry the apparatus; finally, I

My objection applies to the case of an air-thermometer compared with a mercurial thermometer (t. vi. p. 373). It appears to me that this method ought to be rejected for low temperatures, which are so easily obtained stationary by liquid baths. M. Magnus would certainly not have met with such great differences in his experiments on the tension of aqueous vapour at low temperatures, if he had made use of liquid baths.

exhausted the globe for the last time and closed the tube with the lamp. The globe being surrounded with ice, I observed the difference in the level of the two mercurial columns. Admitting that the tension of mercurial vapour is nothing at 0°, the observed difference of level is the simple measurement of the elastic force of the air remaining in the apparatus. The globe is now placed in water, the temperature of which is gradually raised to the boiling-point, and the precautions mentioned above are attended to for obtaining a stationary temperature at the time of observation. The differences of height in the two columns of mercury are then caused by the elastic force of the air remaining in the apparatus and by the tension of the mercurial vapour; this latter may be obtained alone, by deducting from the difference of height observed, the elastic force of the air for the temperature in question, calculated from its elastic force actually observed at zero.

In a first experiment I left purposely a rather notable quantity of air in the apparatus; the elastic force of this air at 0° was found to be 4·22 millimetres. The tensions of the mercurial vapour were found to be—

0°·00 C.	0·000 millimetre.
23°·57	0·068 ...
38°·01	0·098 ...
100°·60	0·555 ...*

In another experiment an almost perfect vacuum was produced by heating to ebullition the mercury in the globe whilst the air was exhausted. The elastic force of the air remaining in the globe was found to be 0·10 millimetre at 0°; the following values were then obtained for the tensions of the mercurial vapour:—

0°·00 C.	0·000 millimetres.
25°·39	0·034 ...
49°·15	0·087 ...
72°·74	0·183 ...
100°·11	0·407 ...

* I made some determinations of the tension of mercurial vapour at more elevated temperatures, by placing the globe in an oil-bath. Towards 200° the experiments became evidently erroneous from distillation of the mercury. Although this was the case, I subjoin the numbers that I obtained; they must only be regarded as approximations :—

100°·6 C.	0·56 millimetre.
146°·3	3·46 ...
177°·9	10·72 ...
200°·5	22·01 ...

These two series of experiments are notably different when the relative values are compared; but the absolute differences are really very small, and may be classed amongst the errors of observation. They suffice, I imagine, to show that the tension of mercurial vapour at 100° C. is about 0·5 millimetre, and that at a temperature of 50° it is scarcely 0·10 millimetre; below 50° it is therefore scarcely worthy of notice, and I considered it unnecessary to introduce the correction into the following Tables:—

TABLE II.

Series A.					
Temperatures.		Mean of temperatures.	Tensions.		Difference.
Therm. No. 8.	Thermom. No. 7.		Observed.	Calculated.	
°	°	°	mm	mm	mm
0·00	0·00	0·00	4·695		
0·00	0·00	0·00	4·665		
0·00	0·00	0·00	4·675		
20·16	20·18	20·17	17·62		
20·14	20·18	20·16	17·64	17·563	+0·08
23·59	23·59	23·59	21·66	..	..
23·57	23·58	23·57	21·62	21·618	−0·00
23·45	23·52	23·48	21·56	..	..
23·45	23·52	23·48	21·59	..	..
28·18	28·26	28·22	28·50	..	..
28·16	28·25	28·20	28·50	28·431	+0·07
28·03	28·09	28·06	28·13	28·200	−0·07
28·07	28·11	28·09	28·31	..	..
31·04	31·11	31·08	33·62	33·559	+0·06
31·04	31·13	31·08	33·62	..	..
33·51	33·63	33·57	38·40	..	..
33·49	33·61	33·55	38·38	38·583	+0·20
36·42	36·53	36·48	45·49	..	..
36·38	36·47	36·43	45·35	..	..
36·35	36·40	36·38	45·19	..	..
36·37	36·42	36·40	45·29	45·183	+0·11
36·54	36·62	36·58	45·76	..	..
36·56	36·62	36·59	45·76	..	..
40·71	40·79	40·75	57·58	57·146	+0·43
40·65	40·72	40·69	57·38	..	..
44·72	44·78	44·75	70·77	70·476	+0·29
49·65	49·75	49·70	90·69	90·617	+0·07
49·65	49·75	49·70	90·74	..	..
Series B.					
0·00	0·00	0·00	4·65	..	..
0·00	0·00	0·00	4·65	..	..
0·00	0·00	0·00	4·65	..	..
19·81	19·83	19·82	17·26	17·199	+0·06
19·82	19·84	19·83	17·26	..	..
19·82	19·85	19·83	17·26	..	..

Table II. continued.

Series B. continued.					
Temperatures.		Mean of temperatures.	Tensions.		Difference.
Thermom. No. 8.	Thermom. No. 7.		Observed.	Calculated.	
°	°	°	mm	mm	mm
22·68	22·73	22·70	20·56	20·513	+0·05
22·69	22·73	22·71	20·58	..	..
22·70	22·74	22·72	20·56	..	..
24·65	24·68	24·67	23·07	..	..
24·65	24·69	24·67	23·10	23·092	+0·01
24·67	24·70	24·69	23·15	..	..
28·83	28·87	28·85	29·50	29·524	−0·02
28·83	28·86	28·84	29·46	..	..
28·83	28·86	28·85	29·48	..	..
33·81	33·84	33·82	39·09	..	..
33·81	33·84	33·82	39·11	39·170	−0·06
18·31	18·35	18·33	15·84	..	..
18·34	18·36	18·35	15·84	15·707	+0·06
18·36	18·37	18·36	15·84	..	..
18·38	18·38	18·38	15·88	..	..
20·99	20·97	20·98	18·60	..	..
21·00	20·98	20·99	18·54	..	..
21·01	20·99	21·00	18·60	18·495	+0·10
25·48	25·47	25·48	24·35	..	..
25·50	25·49	25·49	24·35	..	..
25·52	25·50	25·51	24·41	24·275	+0·15
25·56	25·51	25·53	24·45	..	..
32·16	32·21	32·19	35·86	..	..
32·18	32·21	32·20	35·88	35·737	+0·14
30·94	30·96	30·95	33·42	..	..
30·94	30·98	30·96	33·48	..	..
30·94	30·99	30·97	33·50	33·349	+0·15
30·97	31·00	30·98	33·48	..	..
30·97	31·00	30·98	33·54	..	..
34·18	34·22	34·20	40·22	..	..
34·18	34·23	34·21	40·26	40·031	+0·23
34·19	34·24	34·22	40·28	..	..
37·22	37·25	37·23	47·50	..	..
37·22	37·25	37·23	47·44	47·281	+0·16
37·22	37·25	37·23	47·46	..	..
39·39	39·39	39·39	53·34	53·142	+0·20
39·37	39·41	39·39	53·36	..	..
39·43	39·44	39·43	53·50	..	..
39·44	39·46	39·45	53·76	..	..
42·58	42·63	42·61	63·22	..	..
42·57	42·62	42·60	63·14	63·012	+0·13
42·56	42·61	42·59	63·26	..	..
42·57	42·63	42·60	63·26	..	..
16·49	16·50	16·50	14·05	13·972	+0·08
16·50	16·52	16·51	14·09	..	..
16·54	16·55	16·54	14·07	..	..

Table III.

Series C.

Temperatures. Thermom. No. 7.	Tensions. Observed.	Tensions. Calculated.	Difference.	Temperatures. Thermom. No. 7.	Tensions. Observed.	Tensions. Calculated.	Difference.
°	mm	mm	mm	°	mm	mm	mm
0·00	4·58	..	..	18·11	15·32	..	..
0·00	4·55	..	..	20·28	17·59	..	..
0·00	4·54	..	..	20·23	17·56	..	..
0·00	4·60	..	..	20·25	17·52	17·661	−0·13
0·00	4·58	..	..	20·29	17·56	..	..
0·00	4·56	..	..	20·29	17·64	..	..
0·00	4·58	..	..	20·29	17·63	..	..
11·49	9·96	..	..	22·85	20·52	..	..
11·52	9·97	10·133	−0·16	22·85	20·58	20·699	−0·12
11·54	10·04	..	..	22·86	20·56	..	..
11·54	10·02	..	..	22·88	20·61	..	..
13·84	11·66	..	..	25·59	24·25	..	..
13·84	11·70	11·785	−0·08	25·56	24·22	24·347	−0·12
13·85	11·70	..	..	25·56	24·19	..	..
14·04	11·84	11·939	−0·10	28·14	28·21	28·332	−0·12
14·04	11·82	..	..	28·13	28·15	..	..
14·06	11·85	..	..	30·30	31·92	32·096	−0·17
16·43	13·76	..	..	30·29	31·91	..	..
16·46	13·83	13·937	−0·10	32·49	36·16	36·352	−0·17
19·12	16·34	..	..	32·42	36·01	..	..
19·12	16·40	16·468	−0·07	32·38	36·00	..	..
19·13	16·44	..	..	32·39	35·99	..	..
15·93	13·36	13·475	−0·11	36·13	44·34	44·518	−0·19
15·94	13·37	..	..	36·13	44·32	..	..
18·10	15·32	15·453	−0·13	38·88	51·37	51·704	−0·33
18·09	15·32	..	..	38·86	51·31	..	..

Series D.

0·00	4·69	..	..	13·92	11·84	11·850	−0·01
0·00	4·67	..	..	13·92	11·86	..	..
0·00	4·67	..	..	13·92	11·86	..	..
0·00	4·65	..	..	16·34	13·82	..	..
8·20	8·14	..	..	16·35	13·82	13·840	−0·02
8·24	8·18	..	..	16·36	13·82	..	..
8·27	8·20	8·1640	+0·04	19·88	17·21	..	..
8·28	8·26	..	..	19·88	17·21	17·263	−0·05
9·00	8·58	8·574	+0·01	15·62	13·20	..	..
9·00	8·60	..	..	15·61	13·22	..	..
9·01	8·62	..	..	15·62	13·22	13·212	+0·01
9·02	8·62	..	..	15·62	13·24	..	..
9·04	8·68	..	..				

Series E.

0·00	4·59	..	..	10·11	9·11	..	..
0·00	4·59	..	..	10·11	9·13	..	..
0·00	4·59	..	..	10·11	9·15	9·232	−0·08
6·70	7·27	..	..	13·60	11·54	..	..
6·72	7·27	..	..	13·60	11·56	11·605	−0·04
6·74	7·25	7·361	−0·11	13·60	11·52	..	..
6·77	7·33	..	..	13·60	11·52	..	..
7·39	7·66	7·693	−0·03	14·92	12·55	..	..
7·41	7·64	..	..	14·92	12·57	12·634	−0·06

TABLE III. continued.

SERIES E. continued.

Temperatures. Thermom. No. 7.	Tensions. Observed.	Tensions. Calculated.	Difference.	Temperatures. Thermom. No. 7.	Tensions. Observed.	Tensions. Calculated.	Difference.
°	mm	mm	mm	°	mm	mm	mm
14·91	12·57	..	..	20·54	17·85	..	..
16·54	13·89	..	..	22·84	20·53	..	..
16·55	13·91	..	..	22·84	20·53	20·687	−0·15
16·55	13·87	..	..	22·85	20·55	..	..
16·55	13·91	14·016	−0·10	9·98	9·07	..	..
18·32	15·53	..	..	9·98	9·01	..	..
18·32	15·61	15·667	−0·06	9·98	9·07	..	..
18·32	15·59	..	..	9·98	9·09	9·153	−0·06
20·51	17·81	..	..	17·25	14·57	..	..
20·51	17·81	17·946	−0·13	17·25	14·55	14·650	−0·10

SERIES F.

− 0·37	4·48	4·457	+0·02	−30·59	0·33	..	..
−11·69	1·70	..	..	−28·13	0·47	0·427	+0·04
− 8·11	2·39	2·305	+0·08	−23·95	0·53	..	..
− 4·61	3·19	3·100	+0·09	−19·41	0·88	0·885	0·00
− 7·82	2·46	..	..	−16·83	1·16	1·100	+0·06
− 2·43	3·81	3·739	+0·07	−14·62	1·38	..	..
− 0·83	4·34	..	..	−12·55	1·62	1·581	+0·04

SERIES G.

Temperatures. Th. No. 7. Th. N.	Th. No. 2.	Tensions. Obs.	Calcul.	Difference.	Temperatures. Th. No. 7. Th. N.	Th. No. 2.	Tensions. Obs.	Calcul.	Difference.
°	°	mm	mm	mm	°	°	mm	mm	mm
0·00	0·00	4·61	..	..	−18·41	..	0·98	0·963	+0·02
−27·11	..	0·46	..	..	−16·43	..	1·17	1·138	+0·03
−28·45	..	0·38	..	..	−16·15	..	1·15	..	..
−28·39	..	0·43	..	..	−13·25	..	1·51	..	..
−28·00	..	0·41	0·430	−0·02	−10·67	−10·71	1·88	1·851	+0·03
−27·80	..	0·48	0·438	+0·04	−10·29	−10·31	1·99	..	..
−25·31	..	0·52	..	..	− 7·81	− 7·76	2·51	..	..
−25·00	..	0·52	0·553	−0·03	− 7·56	− 7·59	2·49	2·423	+0·07
−22·74	..	0·71	..	..	− 5·51	− 5·57	2·94	..	..
−21·79	..	0·71	0·724	−0·01	− 5·37	− 5·43	2·96	3·022	−0·06
−21·16	..	0·73	..	..	− 3·72	− 3·75	3·39	3·347	+0·04
−18·69	..	0·93	..	..	− 3·68	− 3·75	3·41	..	..

SERIES H.

0·00	..	4·54	..	..	−30·67	..	0·33	..	..
0·00	..	4·54	..	..	−30·89	..	0·32	0·339	−0·02
0·00	..	4·54	..	..	−30·46	..	0·33	..	..
0·00	..	4·58	..	..	−29·66	..	0·34	..	..
0·00	..	4·58	..	..	−23·23	..	0·61	..	..
0·00	..	4·57	..	..	−23·00	..	0·66	0·654	+0·01
0·00	..	4·58	..	..	−23·71	..	0·57	..	..
−32·84	..	0·27	..	..	−23·51	..	0·59	..	..
−32·78	..	0·28	..	..	−22·27	..	0·66	..	..
−32·26	..	0·29	..	..	−22·10	..	0·66	..	..

Table III. continued.

Series H. continued.

Temperatures.		Tensions.		Difference.	Temperatures.		Tensions.		Difference.
Th. No. 7. Th. N.	Th. No. 2.	Obs.	Calcul.		Th. No. 7. Th. N.	Th. No. 2.	Obs.	Calcul.	
°	°	mm	mm	mm	°	°	mm	mm	mm
−20·49	..	0·76	..	..	− 4·82	− 4·84	3·20	..	..
−20·28	..	0·72	..	..	− 3·64	− 3·64	3·47	..	..
−18·78	..	0·91	0·933	−0·02	− 3·51	− 3·52	3·52	..	..
−18·59	..	0·89	0·948	−0·05	− 2·16	− 2·11	3·91	..	..
−17·32	−17·43	1·01	..	..	− 2·38	− 2·40	3·85	..	..
−17·10	−17·14	1·04	..	..	Th. No. 7.				
−14·36	−14·44	1·34	..	..	+ 2·48	..*	5·41	..	..
−14·17	−14·26	1·38	1·372	+0·01	+ 2·24	..	5·31	..	..
−12·53	−12·59	1·61	..	..	+ 2·30	..	5·32	..	..
−12·26	−12·32	1·63	..	..	+ 3·84	..	5·95	..	..
−10·60	−10·65	1·97	1·862	+0·10	+ 3·85	..	5·97	..	..
−10·47	−10·49	1·99	..	..	+ 5·99	..	6·91	..	..
− 7·84	− 7·90	2·40	2·355	+0·04	+ 5·98	..	6·91	..	..
− 7·64	− 7·73	2·40	..	..	+ 7·96	..	7·94	..	..
− 6·37	− 6·38	2·79	..	..	+ 7·96	..	7·88	..	..
− 6·39	− 6·41	2·82	..	..	+ 7·95	..	7·92	..	..
− 6·20	− 6·24	2·88	..	..	+ 9·71	..	8·87	..	..
− 4·87	− 4·86	3·20	3·037	+0·16	+ 9·70	..	8·87	..	..

Series I.

Temperatures. Thermom. No. 7.	Tensions.		Difference.	Temperatures. Thermom. No. 7.	Tensions.		Difference.
	Observed.	Calculated.			Observed.	Calculated.	
°	mm	mm	mm	°	mm	mm	mm
0·00	4·54	..	..	0·00	4·54	..	..
0·00	4·54	..	..	0·00	4·52	..	..
0·00	4·52	..	..	0·00	4·50	..	..
0·00	4·54	..	..	0·00	4·50	..	..
0·00	4·52	..	..	0·00	4·54	..	..

Series J.

0·00	4·56	..	..	0·00	4·52	..	−0·08
0·00	4·53	..	..	7·61	7·64	7·808	−0·168
0·00	4·56	..	..	9·93	8·94	9·122	−0·182
0·00	4·54	..	..	12·34	10·46	10·693	−0·233
0·00	4·52	..	..	16·42	13·60	13·902	−0·302

Series K.

0·00	4·54	..	..	7·61	7·63	..	..
0·00	4·54	..	..	7·61	7·65	7·808	−0·158
0·00	4·52	..	..	9·93	8·95	9·122	−0·172
0·00	4·54	..	..	9·93	8·93	..	..
0·00	4·54	..	..	12·34	10·47	10·692	−0·222
0·00	4·56	..	..	12·34	10·45	..	..
0·00	4·54	..	..	16·42	13·58	..	..
0·00	4·56	..	..	16·42	13·62	13·901	−0·281

TABLE III. continued.

SERIES L.

Temperatures. Thermom. No. 7.	Tensions. Observed.	Tensions. Calculated.	Difference.	Temperatures. Thermom. No. 7.	Tensions. Observed.	Tensions. Calculated.	Difference.
°	mm	mm	mm	°	mm	mm	mm
0·00	4·66	..	..	24·36	22·65	22·668	−0·02
0·00	4·67	..	..	27·09	26·64	26·646	0·00
0·00	4·64	..	..	27·09	26·68	..	..
0·00	4·62	..	..	28·27	28·58	..	..
0·00	4·64	..	..	28·28	28·65	28·564	+0·09
0·00	4·66	..	..	26·87	26·36	26·31	+0·05
0·00	4·67	..	..	26·87	26·37	..	..
0·00	4·66	..	..	33·71	38·92	..	..
0·00	4·66	..	..	33·70	38·87	38·909	−0·04
9·77	9·03	..	..	37·07	46·83	..	..
9·80	9·02	9·044	−0·02	37·06	46·89	46·845	+0·04
9·83	9·07	..	..	37·06	46·82	..	..
12·75	11·00	..	..	41·03	57·97	58·002	−0·03
12·75	10·98	10·982	−0·00	41·03	58·06	..	..
15·63	13·13	..	..	41·02	57·97	..	..
15·63	13·18	13·22	−0·04	44·08	68·21	..	..
18·94	16·25	..	..	44·08	68·24	..	..
18·97	16·27	16·284	−0·01	44·08	68·09	68·072	+0·02
18·97	16·29	..	..	35·13	42·29	42·129	+0·16
21·37	18·77	..	..	35·13	42·35	..	..
21·37	18·82	18·918	−0·10	35·13	42·27	..	..
24·36	22·64	..	..				

SERIES M.

0·00	4·66	..	..	26·68	26·08	26·012	+0·07
0·00	4·66	..	..	26·68	26·10	..	..
0·00	4·66	..	..	36·15	44·54	..	..
25·69	24·51	..	..	36·17	44·63	..	..
25·69	24·54	24·533	−0·01	36·17	44·65	44·615	+0·03
35·87	43·86	..	..	44·39	69·31	..	..
35·87	43·90	43·886	+0·01	44·38	69·25	69·142	+0·13
43·66	66·67	..	..	51·22	97·41	97·718	−0·30
43·66	66·60	66·602	0·00	51·21	97·39	..	..
43·62	66·57	..	..	53·61	109·90	..	..
49·58	90·10	90·076	+0·02	53·63	109·96	109·954	0·00
49·58	90·04	..	..	53·66	110·16	..	..
49·58	90·04	..	..	58·34	137·29	..	..
14·37	12·25	12·220	+0·03	58·38	137·78	..	..
14·40	12·30	..	..	58·37	137·66	137·632	+0·03
26·69	26·12	..	..				

The preceding Tables contain all the experiments which I have made upon the elastic forces of aqueous vapour at low temperatures; but I do not look upon all the series as being equally accurate. Thus the series J. K. is but little trustworthy, merely because the differences between the calculated and observed numbers increase constantly with the temperature.

IV. The methods which I have described in the foregoing chapters are only applicable for temperatures below 60° or 70°; at higher temperatures the water divides itself so quickly into un-

equally heated strata, that a constant agitation is required to prevent this separation from taking place; these methods become on that account quite impracticable for temperatures above 100°.

I had recourse for elevated temperatures to a well-known mode of procedure, which has been adopted by several philosophers, and especially by MM. Arago and Dulong. This method consists in ascertaining the temperature at which water boils under known pressures; it possesses the advantage of being applicable under the most elevated pressures, and gives very accurate results when properly conducted.

In the apparatus of MM. Arago and Dulong the water did not actually boil (*Annales de Chimie et de Physique*, 2me Series, vol. xliii. p. 74); its elastic force increased by the action of heat up to a certain maximum, which was determined by an air manometer, at the same time that the thermometers immersed in the vapour and in the liquid of the heating vessel were observed; at other times the manometer and thermometers were simultaneously observed whilst the temperature was still ascending and approached its maximum. It is to be feared that by this mode of operating, the thermometers, which are necessarily a little behind the temperature of the vapour, do not attain the same degree which it possesses at the moment when their maximum is noted.

The error which could arise from this cause is probably very small, or even imperceptible in experiments made under great pressures, because in this case a very small difference of temperature corresponds to a great alteration in the elastic force; but the error would probably not be imperceptible at feeble pressures, for instance at such as are inferior to the pressure of the atmosphere. But it is easy to render this mode of proceeding unobjectionable, by so arranging the experiment that the conditions are quite identical with those under which water is boiled under the ordinary pressure of the atmosphere for fixing the point of 100° in thermometers; and the temperature at which water boils under different pressures can be determined with the same precision. For this purpose water is made to boil in a vessel communicating with a pretty considerable space, in which the air may be compressed or dilated at pleasure; this air forms an artificial atmosphere, exercising pressure upon the surface of the heated liquid. Thus a boiling temperature is obtained as perfectly constant as that which water presents when boiling

freely in air; and this temperature can be kept stationary as long as is required. The apparatus which I arranged to suit these conditions is represented in fig. 6. It consists of a retort of copper, A, closed by a cover screwed to it. This cover carries four tubes closed at bottom; two of these tubes descend nearly to the bottom of the retort, the other two only reach to the middle. These tubes, which are 7 millimetres internal diameter, and about 1 millimetre thick, are surrounded by a very thin hollow copper cylinder, attached to the lid and pierced in the upper part by the holes *o, o, o*. The neck of the retort is connected with a tube T T′, about 1 metre in length, enclosed within a hollow cylinder of copper, through which a constant stream of cold water is kept up; this tube is in communication with a copper globe B, having a capacity of 24 litres, and enclosed in a vessel, V V′, filled with water at the surrounding temperature. The globe at its upper part is supplied with a connecting piece having two arms; into one of these arms *x s*, the tube *e g h* of the apparatus fig. 2, is cemented when experiments are to be made at lower pressures than those of the atmosphere, or the tube *p q* of the apparatus fig. 8, when the experiments are to be conducted at higher pressures. The second arm communicates by means of the leaden tube *t t′*, either with an air-pump for rarefying the air in the apparatus, or with a forcing-pump, if the air is to be condensed.

The four iron tubes are filled with mercury within a few centimetres of their upper end; mercurial thermometers are placed in these tubes; the bulbs of these thermometers descend to the bottom of the tubes, two of these thermometers are thus immersed in water, and two in vapour.

The air is exhausted in the apparatus, so as to leave but a very slight pressure. The water is heated to boiling; the vapour soon condenses in the condensing-tube T T′, and falls again into the retort. The pressure at which ebullition takes place is measured by the difference in the height of the mercury in the tube and the level of the mercury in the barometer. The column of mercury sustained in the tube which communicates with the globe is never absolutely stationary; it has nearly always a slight oscillatory motion, but this motion only occurs within an extremely minute space, not exceeding one-tenth of a millimetre, when the fire is properly regulated under the retort. The observer following the meniscus under the thread of the telescope of the cathetometer can easily observe the meniscus when it is

absolutely stationary; the position which the meniscus then occupies is exactly the mean of those extreme positions which it took during its very small oscillations. The barometer dipping into the same cup does not exhibit sensible oscillations, so that it can be conveniently read off after the observations on the meniscus.

A second observer reads at a distance with a telescope the thermometers immersed in the retort; errors of parallax are thus avoided in the reading.

In this manner a certain number of determinations were made at the same pressure, allowing between two consecutive determinations an interval of eight or ten minutes to elapse; it was thus easy to perceive the perfect steadiness of the temperatures indicated by the thermometers for the same pressure, and to be convinced, that the least change in the pressure was indicated immediately by a corresponding variation in the temperature.

For obtaining a still greater pressure in the apparatus, the stop-cock r was opened with caution, and a quantity of air admitted sufficient to establish the desired pressure.

Thus the temperatures at which water boils were obtained successively from the lowest pressures up to that of the atmosphere. This latter was measured by the barometer attached to the apparatus, by the operation described at page 570.

For ascertaining the temperatures at which water boils under higher pressures than those of the atmosphere, the apparatus was arranged in the manner shown at fig. 6; that is to say, the measuring apparatus of fig. 2 was replaced by that of fig. 8, and the tube $t\,t'$ was brought into connection with a forcing-pump. The tube $m\,n$ is about 4 metres in length and 14 millimetres interior diameter; it is fixed to a long board kept perfectly vertical. Three thermometers with large bulbs, placed at convenient distances, show the mean temperature of the column of mercury in the tube $m\,n$.

By means of the forcing-pump the requisite pressure is established in the apparatus. This pressure is measured by the height of the barometer, added to the height of mercury representing the difference between the mercurial levels in the tubes $m\,n$ and $p\,q$. The determination of this last height requires some precautions if great exactitude is aimed at. In the actual position of the apparatus both columns of mercury oscillate in the tubes $m\,n$ and $p\,q$. These oscillations take place only within very narrow limits, and they are often only perceptible by means of the telescope of the cathetometer, which magnifies consi-

derably: however, considerable errors of measurement might arise, if the meniscus in the tube *m n* and the meniscus in the tube *p q* were read off successively with the same cathetometer. Besides, this operation would be impossible when the difference of level surpassed 1 metre, which is the greatest length of the range of our cathetometers: therefore two cathetometers were used at a time. Each of these instruments followed one of the menisci; and it thus became easy to observe the perfectly corresponding positions of the two menisci, choosing that moment when the extent of the oscillations was very small (one-tenth of a millimetre) about one point of equilibrium. The observations were made simultaneously by two observers, on a signal being given by one of them. The two cathetometers were regulated to the same fixed point traced upon the tube *p q*, very near the position into which the meniscus was constantly brought.

At the same time there were traced on the tube *m n*, at intervals of $0^{m}{\cdot}90$, fixed points, the distances between which had been read off a great many times by means of the cathetometer. Between these different determinations of one and the same length, more than 3 metres, there was never found a difference amounting to one-tenth of a millimetre; which proves sufficiently the exactitude of the mode of measurement. I still wished to ascertain, by direct measurements, if the scales of the two cathetometers were identical, and what degree of precision could be attained by this method of observation. For this purpose I placed the two instruments opposite to each other, in such a position that by means of the telescope of the one the divisions of the other could be read in the most distinct manner, and *vice versâ*. I then took, proceeding from 5 to 5 centimetres at a time, the divisions of one of the instruments by means of the micrometric apparatus of the other. In this manner I obtained in no part of the whole range of 1 metre a difference amounting to one-twentieth of a millimetre. To obtain a like precision in the measurements, it is evident that the instruments ought to be constructed in the most perfect manner; the telescopes should not have a too great focal length ($0^{m}{\cdot}30$), and in particular the levels of the telescopes should be extremely delicate. The levels of the cathetometers of M. Gambey indicate inclinations of one second. The verniers give immediately the one-fiftieth of a millimetre, and the $\frac{1}{100}$th is easily estimated.

The mercurial thermometers which I employed in these experiments were ordinary thermometers with straight stems; one

portion of the mercurial columns was necessarily outside the cover of the retort, and had not the temperature of the vapour; a correction was consequently required to be made for it. This correction would have been easily made if the mean temperature of the columns had been known with sufficient exactitude. When the stem is in the open air, the temperature of the different points of the column outside the retort varies according to the distance at which those points are from the lid. To avoid all sources of uncertainty, MM. Arago and Dulong made use of thermometers the stems of which were bent at right angles, immediately on leaving the iron tubes, and enclosed in horizontal glass tubes in which a current of cold water circulated, the temperature of which could be ascertained by a small thermometer.

By means of this artifice the length of the column, the temperature of which is uncertain, is very much diminished; but there remains always a considerable portion of the stem at the place of bending which cannot be surrounded by water, and of which the temperature remains unknown. Thermometers bent in this manner are besides, for many other important reasons, inconvenient. That their bore may be exact, it is necessary that they have their scale only on the horizontal part of the stem; consequently the correction must be made for a very considerable number of degrees. The position of the fixed points is likewise more difficult to determine accurately in bent thermometers than in such as have straight stems. These considerations determined me to employ thermometers with straight stems, so placed, that only a portion of the scale extended beyond the retort. A small thermometer, placed in the middle of the columns which were not immersed, indicated a temperature which was taken as the expression of the mean temperature of the mercurial columns not immersed. It remained to be ascertained whether the corrections made in this manner were sufficiently exact, or whether they ought to be modified in order to obtain their real value. To decide this question I made the following experiments:—

A very delicate thermometer, perfectly free from air and having a range from 0° to 110°, had a bulb at the extremity of its stem, into which a portion of its mercury could be poured*. With the greatest care in melting ice, the freezing-point on this ther-

* The invention of this thermometer, which has very lately been claimed by a M. Walferdin, is really due to Wollaston the astronomer, who first suggested it.—Edit.

mometer was ascertained, as was the 100th degree by the vapour of boiling water, the stem being entirely surrounded by vapour. The same thermometer was immediately placed in one of the iron tubes of the retort in which water was boiling under the ordinary pressure of the atmosphere; a portion of the stem in this case extended beyond the cover of the retort. The temperature indicated by the thermometer under these circumstances was corrected for that portion of the column not immersed, by taking as basis the temperature indicated by a small thermometer, the reservoir of which was placed at the height of the middle of the column; it was found to be identically the same as that previously obtained in the apparatus where the entire stem was immersed in the vapour. This experiment was not conclusive for demonstrating the exactitude of the correction, for one must have admitted in that case that the mercurial thermometer, immersed in the iron tube, indicated exactly the temperature of the vapour in the retort. This last result being demonstrable in a direct manner, I did not neglect doing it. For that purpose, I forced a portion of the mercury of our thermometer out of the stem, and, by inclining the stem, brought it into the reservoir at the top; so that the thermometer being now again immersed in the iron tube of the retort, whilst the water was boiling under the ordinary pressure of the atmosphere, the mercury remained stationary at a height of some millimetres above the cover. I observed with the greatest care, by means of the horizontal telescope of a cathetometer, the division marked upon the thermometer; I then plunged the instrument into the apparatus which was used for determining the point 100° of the thermometers, and read off in the same manner the division at which the column of mercury stood. I found it quite impossible to perceive the least difference in the temperatures indicated under these different circumstances by the thermometer, although 1° of temperature took up six divisions of the scale.

The two preceding experiments together show,—1st, that thermometers, under the circumstances in which they are placed in the apparatus fig. 7, take the temperature of the vapour; 2nd, that the mode of correction which I adopted for that portion of the stem which was not immersed is exact, for the temperature of 100°. The maximum of correction required for my thermometers amounted to 0°·35. I have assumed that the same mode of correction is applicable to temperatures below 100°.

The thermometers employed in the experiments which were made at inferior pressures to those of the atmosphere ranged only from 0° to 100°; they had from six to eight divisions for each degree; it was therefore easy to observe with accuracy the $\frac{1}{60}$th of a degree. The four thermometers employed in the experiments with high pressures had a range from 0° to about 240°. The centigrade degree was equivalent to from 2·5 to 3 divisions of their scale. All these instruments were graduated and verified with the greatest care.

For correcting those portions of the column not immersed in the experiments under high pressure, the following experiments were made:—

The water in the retort was made to boil under a certain pressure greater than that of the atmosphere; three of the four thermometers were immersed in the iron tubes; in the fourth iron tube, the thermometer having a bulb at the upper end was placed, with the mercury so separated that the column should remain stationary at a few millimetres above the cover, and required consequently no correction; the indications of the four thermometers were then read off. To be enabled to calculate the temperature indicated by the double-bulbed thermometer, it was only necessary to know the position of the 100° point on the thermometer; this position was determined in a direct manner by immersing the thermometer in the vapour of boiling water at the pressure of the atmosphere.

The temperature of the thermometer with the two bulbs requiring no correction being known, as likewise that of the other thermometers which required correction for those portions of their columns above the retort, it was easy to see whether the mode of correction employed brought uniformity into all the indications. It may be well to mention, that the portions of the stems not immersed were of various lengths in the different thermometers, and required consequently very different absolute corrections.

These experiments were made at about the temperatures of 110°, 120°, 130°, and 140°: it was observed, that between these limits of temperature, corrections being made for the stems, on the supposition that their mean temperature was indicated by a mercurial thermometer, the reservoir of which occupied a medium position, the thermometers never differed from the thermometer with two bulbs more than 0°·2. These differences may be

attributable, at least in part, to the inequality of range in the instruments. I have admitted therefore, that the correction made for the portion of the columns not immersed, upon the principle which has been explained, may be considered sufficiently exact for temperatures up to 145°.

I have collected in the following tables the results which were obtained. The temperatures indicated by the thermometers immersed in the liquid are given apart from those indicated by the thermometers immersed in the vapour. It will be seen, that when water boils at low pressures, the thermometer immersed in the water takes a temperature considerably above that one which is immersed in the vapour: the difference amounts to 0°·7 at very weak pressures; it diminishes in proportion as the temperature of the boiling liquid rises, that is to say, in proportion as ebullition is effected at a higher pressure, and it ceases altogether when that occurs at the pressure of the atmosphere. Nor in the more elevated pressures is a more perceptible difference observable: this it was that induced me to inscribe in Table V., which relates to these pressures, the mean of the four thermometers.

I purposely began this series of experiments at very feeble pressures, to enable me to compare the results which it gave with those which were obtained for the same temperatures by the methods described in the preceding chapters. I have discovered as perfect a correspondence as could have been desired; it is evident at the same time that for low temperatures the first methods are preferable.

TABLE IV.

SERIES N.								
Thermometers in the liquid.		Mean.	Thermometers in the vapour.		Mean.	Tensions.		Difference.
O.	A.		No. 8.	No. 7.		Observed.	Calculated.	
°	°	°	°	°	°	mm	mm	mm
43·55	43·55	43·55	42·90	42·82	42·86	64·13	63·896	+0·25
43·64	43·55	43·59	42·89	42·83	42·86	64·13	..	..
43·64	43·46	43·55	42·91	42·83	42·87	64·12	..	..
49·49	49·50	49·495	48·95	48·99	48·97	87·59	..	..
49·49	49·52	49·50	48·98	49·02	49·00	87·57	..	..
49·53	49·54	49·535	48·98	49·00	48·99	87·55	87·455	+0·10
54·06	54·01	54·03	53·44	53·51	53·48	109·52	..	..
54·04	54·03	54·035	53·45	53·51	53·48	109·60	..	..
54·06	54·04	54·05	53·46	53·51	53·49	109·64	..	..

Table IV. continued.

Series N. continued.								
Thermometers in the liquid.		Mean.	Thermometers in the vapour.		Mean.	Tensions.		Difference.
O.	A.		No. 8.	No. 7.		Observed.	Calculated.	
°	°	°	°	°	°	mm	mm	mm
54·07	54·05	54·06	53·46	53·51	53·49	109·64	109·21	+0·43
54·06	54·04	54·05	53·46	53·51	53·49	109·66	..	..
57·37	57·38	57·375	56·78	56·86	56·82	128·47	..	..
57·38	57·38	57·38	56·78	56·84	56·81	128·49	128·091	+0·40
57·40	57·37	57·385	56·78	56·84	56·81	128·43	..	..
57·37	57·37	57·37	56·78	56·84	56·81	128·43	..	..
61·31	61·39	61·35	60·84	60·89	60·86	155·18	..	..
61·34	61·39	61·36	60·84	60·88	60·86	155·16	154·836	+0·32
61·38	61·47	61·42	60·88	60·93	60·90	155·40	..	..
66·25	66·34	66·30	65·83	65·89	65·86	194·62	194·280	+0·34
66·25	66·34	66·30	65·83	65·89	65·86	194·62	..	..
66·25	66·35	66·30	65·83	65·89	65·86	194·62	..	..
71·95	72·37	72·16	71·75	71·77	71·76	251·73	..	..
71·95	72·38	72·165	71·74	71·77	71·76	251·73	251·463	+0·27
71·95	72·39	72·17	71·74	71·78	71·76	251·79	..	..
76·69	76·83	76·76	76·49	76·47	76·48	306·71	306·908	−0·19
76·69	76·81	76·75	76·50	76·48	76·49	306·71	..	..
76·68	..	..	76·46	76·44	76·45	306·47	306·524	−0·05
76·68	76·79	76·73	76·46	76·43	76·45	306·41	..	..
80·28	80·40	80·34	80·13	80·10	80·115	356·00	..	..
80·28	80·40	80·34	80·13	80·10	80·115	356·00	356·229	−0·23
80·28	80·40	80·34	80·12	80·09	80·105	356·00	..	..
83·24	83·33	83·28	83·08	83·06	83·07	401·28	..	..
83·24	83·33	83·28	83·07	83·05	83·06	401·30	..	..
83·24	83·33	83·28	83·07	83·05	83·06	401·30	401·057	+0·24
83·24	83·32	83·28	83·07	83·04	83·06	401·30	..	..
86·81	86·80	86·80	86·66	86·65	86·65	462·27	..	..
86·81	86·83	86·82	86·66	86·66	86·66	462·26	..	..
86·81	86·85	86·83	86·66	86·67	86·67	462·34	462·257	+0·08
86·81	86·88	86·85	86·67	86·67	86·67	462·34	..	..
89·93	89·96	89·95	89·83	89·83	89·83	522·02	..	..
89·94	89·98	89·96	89·83	89·83	89·83	522·02	522·058	−0·04
89·94	89·90	89·92	89·84	89·83	89·83	522·00	..	..
92·32	92·24	92·28	92·19	92·17	92·18	569·79	..	..
92·31	92·22	92·26	92·18	92·15	92·17	569·79	..	..
92·32	92·21	92·26	92·18	92·17	92·17	569·71	..	..
92·32	92·28	92·30	92·20	92·21	92·20	569·83	..	..
92·32	92·28	92·30	92·20	92·19	92·20	569·83	571·033	−1·20
94·11	94·05	94·08	94·08	93·99	94·04	610·24	..	..
94·10	94·01	94·05	94·04	93·97	94·00	610·54	..	..
94·10	94·08	94·09	94·05	94·00	94·02	610·54	..	..
94·10	94·08	94·09	94·04	94·01	94·02	610·54	611·194	−0·65
95·79	95·77	95·78	95·77	95·74	95·75	651·64	..	..
95·79	95·73	95·76	95·76	95·72	95·74	651·34	651·288	+0·05
95·79	95·74	95·78	95·77	95·73	95·74	651·32	..	..
96·93	96·83	96·88	96·83	96·82	96·83	677·88	..	..
96·92	96·83	96·88	96·85	96·82	96·84	677·98	678·060	−0·08
96·92	96·86	96·89	96·89	96·85	96·87	677·92	..	..
96·92	96·89	96·90	96·87	96·82	96·84	677·88	..	..
98·75	98·82	98·78	98·76	98·70	98·73	727·07	726·205	+0·86
98·76	98·85	98·80	98·76	98·70	98·73	727·19	..	..
100·20	100·16	100·18	100·20	100·13	100·17	765·70	765·10	+0·60

TABLE IV. continued.

SERIES O.								
Thermometers in the liquid.		Mean.	Thermometers in the vapour.		Mean.	Tensions.		Difference.
O.	A.		No. 8.	No. 7.		Observed.	Calculated.	
°	°	°	°	°	°	mm	mm	mm
47·84	47·56	47·70	47·16	47·17	47·16	80·19	79·64	+0·55
47·84	47·57	47·70	47·14	47·18	47·16	80·19	..	..
62·40	62·40	62·40	62·06	62·01	62·04	163·44	163·469	−0·02
62·40	62·41	62·40	62·06	62·01	62·04	163·44	..	..
62·40	62·40	62·40	62·08	62·00	62·04	163·44	..	..
71·75	71·76	71·75	71·42	71·45	71·44	248·17	248·045	+0·12
71·77	71·77	71·77	71·44	71·46	71·45	248·17	..	..
71·75	71·77	71·76	71·42	71·46	71·44	248·17	..	..
79·20	79·22	79·21	78·94	78·96	78·95	340·35	339·794	+0·56
79·20	79·22	79·21	78·94	78·95	78·95	340·27	..	..
79·20	79·21	79·20	78·94	78·95	78·95	340·27	..	..
84·34	84·35	84·35	84·15	84·15	84·15	419·72	..	..
84·34	84·34	84·34	84·15	84·15	84·15	419·62	418·765	+0·86
84·34	84·34	84·34	84·15	84·14	84·15	419·64	..	..
84·34	84·35	84·35	84·15	84·15	84·15	419·64	..	..
87·60	87·57	87·58	87·47	87·43	87·45	476·38	..	..
87·62	87·59	87·60	87·50	87·45	87·48	476·52	477·010	−0·49
87·62	87·60	87·61	87·52	87·47	87·49	476·50	..	..
87·64	87·59	87·62	87·50	87·46	87·48	476·44	..	..
89·94	..	89·94	89·75	89·75	89·75	519·59	..	..
89·94	89·86	89·90	89·75	89·75	89·75	519·57	520·468	−0·90
89·92	89·82	89·87	89·73	89·74	89·73	519·37	..	..
91·48	91·38	91·43	91·30	91·32	91·31	550·18	..	..
91·48	91·34	91·41	91·30	91·32	91·31	550·36	..	..
91·48	91·34	91·41	91·28	91·30	91·29	550·30	551·794	−1·49
91·46	91·34	91·40	91·28	91·30	91·29	550·22	..	..
91·48	91·34	91·41	91·26	91·30	91·28	550·22	..	..
92·58	92·28	92·43	92·41	92·37	92·39	573·96	..	..
92·58	92·28	92·43	92·41	92·37	92·39	573·96	..	..
92·58	92·29	92·44	92·41	92·37	92·39	573·98	575·120	−1·14
93·74	93·67	93·70	93·62	93·59	93·60	601·98	..	..
93·80	93·65	93·72	93·67	93·63	93·65	601·96	..	..
93·80	93·65	93·72	93·67	93·65	93·66	601·96	..	..
93·79	93·65	93·72	93·69	93·63	93·66	602·02	603·070	−1·05
95·03	94·84	94·93	94·83	94·87	94·85	628·65	..	..
95·03	94·85	94·94	94·85	94·87	94·86	628·61	..	..
95·01	94·85	94·93	94·83	94·87	94·85	628·61	630·277	−1·66
95·92	95·83	95·87	95·84	95·80	95·82	653·22	..	..
95·92	95·81	95·87	95·84	95·79	95·82	653·01	..	..
95·92	95·83	95·87	95·82	95·78	95·80	652·97	652·725	+0·25
95·92	95·80	95·86	95·80	95·77	95·79	652·95	..	..
96·93	96·77	96·85	96·76	96·77	96·76	676·24	..	..
96·91	96·76	96·83	96·76	96·77	96·76	676·18	676·083	+0·10
96·91	96·75	96·83	96·74	96·76	96·75	676·14	..	..
98·77	98·75	98·76	98·66	98·66	98·66	724·38	724·373	0·00
98·75	98·76	98·76	98·66	98·67	98·66	724·18	..	..
100·23	100·10	100·16	100·25	100·12	100·18	765·11	765·114	0·00

TABLE IV. continued.

Thermometers in the liquid. O.	Thermometers in the liquid. A.	Mean.	Thermometers in the vapour. No. 8.	Thermometers in the vapour. No. 7.	Mean.	Tensions. Observed.	Tensions. Calculated.	Difference.
°	°	°	°	°	°	mm	mm	mm
SERIES P.								
47·73	47·87	47·80	47·00	47·10	47·05	79·69	79·294	+0·40
47·59	47·75	47·69	46·92	47·01	46·96	79·53	78·95	+0·58
52·72	52·92	52·82	52·16	52·15	52·16	102·82	102·34	+0·48
53·01	53·18	53·09	52·49	52·47	52·48	104·79	103·96	+0·83
62·93	63·20	63·06	62·52	62·56	62·54	167·93	167·249	+0·68
63·14	63·37	63·25	62·73	62·76	62·75	169·32	168·86	+0·46
70·60	70·88	70·74	70·28	70·28	70·28	236·62	235·94	+0·68
70·87	71·17	71·02	70·60	70·60	70·60	239·78	239·23	+0·55
75·45	75·62	75·53	75·18	75·18	75·18	291·31	290·70	+0·61
75·57	75·85	75·71	75·32	75·32	75·32	293·12	292·34	+0·78
79·69	79·91	79·80	79·50	79·51	79·50	348·16	347·50	+0·66
82·96	83·16	83·06	82·81	82·78	82·80	397·74	396·93	+0·81
85·03	85·20	85·11	84·89	84·90	84·90	432·29	431·34	+0·95
90·83	90·87	90·85	90·70	90·67	90·68	539·51	539·20	+0·31
93·73	93·71	93·72	93·70	93·60	93·65	604·08	602·87	+1·21
96·84	96·80	96·82	96·82	96·69	96·76	676·29	676·08	+0·21
99·98	100·02	100·00	99·90	99·87	99·87	760·48	757·13	+3·35*
SERIES Q.								
91·25	91·15	91·20	91·06	91·10	91·08	548·01	..†	..
91·25	91·15	91·20	91·06	91·09	91·08	548·01	547·43	+0·58
91·25	91·15	91·20	91·07	91·10	91·09	547·91	..	..
94·34	94·18	94·26	94·15	94·14	94·15	614·96	..	..
94·34	94·19	94·27	94·15	94·15	94·15	614·94	614·15	+0·79
94·33	94·21	94·27	94·18	94·17	94·18	614·90	..	..
96·58	96·51	96·55	96·52	96·49	96·50	668·66	669·69	−1·03
96·58	96·52	96·55	96·50	96·49	96·50	668·64	..	..
97·03	96·91	96·97	96·95	96·87	96·91	679·76	..	..
97·03	96·89	96·96	96·92	96·86	96·89	679·56	..	..
97·03	96·90	96·96	96·92	96·87	96·90	679·46	679·55	−0·11
97·03	96·91	96·97	96·92	96·87	96·90	679·44	..	..
97·52	97·46	97·49	97·46	97·42	97·44	692·92	..	..
97·52	97·43	97·48	97·44	97·40	97·42	692·62	692·54	+0·08
97·52	97·42	97·47	97·41	97·38	97·40	692·62	..	..
97·51	97·43	97·47	97·42	97·40	97·41	692·48	..	..
98·45	98·49	98·47	98·39	98·41	98·40	717·85	717·60	+0·25
98·45	98·49	98·47	98·40	98·40	98·40	717·83	..	..
98·45	98·49	98·47	98·39	98·40	98·40	717·81	..	..
99·15	99·18	99·16	99·08	99·07	99·07	734·82	735·16	−0·34
99·15	99·17	99·16	99·10	99·06	99·08	734·74	..	..
99·15	99·17	99·16	99·08	99·05	99·06	734·70	..	..
99·62	99·57	99·60	99·59	99·56	99·58	748·90	748·76	+0·14
99·62	99·57	99·60	99·61	99·57	99·59	748·92	..	..
99·62	99·57	99·60	99·59	99·57	99·58	748·84	..	..

* This last experiment is evidently erroneous; the retort communicated directly with the external atmosphere.

† The calculated tensions were determined by the formula (A.), taking the mean of the temperatures indicated by the two thermometers immersed in the vapour.

TABLE V.

SERIES R.

Thermometers in the liquid.		Mean.	Thermometers in the vapour.		Mean.	Mean of four therm.	Tensions.		Difference.
No. 10.	No. 12.		No. 9.	No. 11.			Observed.	Calculated.	
°	°	°	°	°	°	°	mm	mm	mm
99·85	99·82	99·83	99·80	99·83	99·82	99·83	751·61	..	..
100·74	100·68	100·71	100·72	100·71	100·71	100·71	776·03	..	..
100·82	100·72	100·77	100·72	100·71	100·71	100·74	777·09	779·86	−2·77
105·14	105·06	105·10	105·07	105·06	105·06	105·08	904·87	905·45	+0·58
105·14	105·06	105·10	105·07	105·06	105·06	105·08	904·32	..	..
111·84	111·73	111·78	111·68	111·72	111·70	111·74	1131·60	1131·35	+0·25
111·84	111·73	111·78	111·68	111·72	111·70	111·74	1131·34	..	..
116·12	116·08	116·10	116·07	116·01	116·04	116·07	1302·37	1302·37	0·00
116·06	116·08	116·07	116·07	116·01	116·04	116·06	1302·23	..	..
122·72	122·67	122·70	122·56	122·50	122·53	122·59	1601·25	1600·52	+0·73
122·72	122·67	122·70	122·56	122·50	122·53	122·59	1601·25	..	..
128·51	128·57	128·54	128·53	128·41	128·47	128·50	1925·20	1918·02	+7·18
128·51	128·57	128·54	128·55	128·37	128·46	128·50	1925·48	..	..
128·63	128·69	128·66	128·66	128·49	128·57	128·62	1931·14	..	..
128·59	128·61	128·60	128·62	128·45	128·53	128·57	1929·36	..	..
131·38	131·39	131·38	131·38	131·23	131·30	131·35	2094·69	..	..
131·42	131·43	131·42	131·42	131·27	131·34	131·38	2096·47	2090·72	+5·75
135·70	135·71	135·70	135·75	135·55	135·65	135·68	2373·03	..	..
135·70	135·71	135·70	135·75	135·55	135·65	135·68	2373·03	2372·33	+0·70
138·37	138·36	138·36	138·28	138·20	138·24	138·30	2561·73	..	..
138·37	138·40	138·39	138·32	138·20	138·26	138·32	2561·50	2560·18	+1·32
140·92	140·91	140·91	141·01	..	..	140·95	2758·69	..	..
140·88	140·91	140·90	141·01	..	..	140·93	2756·17	2757·93	−1·76
143·88	143·93	143·90	144·10	143·76	143·93	143·92	2997·75	..	..
143·84	143·85	143·85	143·98	143·68	143·83	143·84	2992·79	2991·67	+1·12
145·69	145·67	145·68	145·68	145·58	145·63	145·65	3150·42	..	..
145·73	145·67	145·70	145·68	145·60	145·64	145·67	3149·41	3148·28	+1·13
145·73	145·71	145·72	145·72	145·60	145·66	145·69	3149·73	..	..
147·50	147·49	147·50	147·54	147·35	147·45	147·48	3307·33	3308·86	−1·53
147·50	147·49	147·50	147·54	147·35	147·45	147·48	3306·52	..	..
147·50	147·49	147·50	147·54	147·35	147·45	147·48	3306·39	..	..

SERIES S.

128·34	128·28	128·31	128·44	128·19	128·32	128·32	1908·81	1907·64	+1·17
128·34	128·28	128·31	128·44	128·19	128·32	128·32	1910·09	..	..
128·27	128·24	128·25	128·40	128·15	128·28	128·27	1908·90	..	..
126·17	126·15	126·16	126·26	126·13	126·20	126·18	1794·11	1788·76	+5·35
126·17	126·15	126·16	126·24	126·13	126·18	126·17	1793·47	..	..
126·17	126·15	126·16	126·26	126·15	126·20	126·18	1793·12	..	..
122·90	122·87	122·88	123·02	122·82	122·90	122·89	1620·04	..	..
122·82	122·83	122·82	122·98	122·78	122·88	122·85	1618·54	1615·01	+3·53
122·82	122·83	122·82	122·94	122·78	122·86	122·84	1618·70	..	..
119·24	119·22	119·23	119·36	119·19	119·27	119·25	1447·30	1442·28	+5·02
119·24	119·22	119·23	119·36	119·19	119·27	119·25	1447·37	..	..
117·50	117·37	117·43	117·52	117·41	117·46	117·45	1364·90	1361·68	+3·22
117·46	117·41	117·43	117·52	117·37	117·44	117·44	1364·78	..	..
110·68	110·72	110·70	110·67	110·64	110·65	110·68	1095·44	1091·58	+3·86
110·68	110·68	110·68	110·67	110·64	110·65	110·66	1094·68	..	..
99·74	99·69	99·72	99·78	99·80	99·79	99·75	753·96	..	..

The calculated tensions were determined by the formula (C.), taking the mean temperature given by the four thermometers.

Table V. continued.

Series T.*				
Thermometer in the vapour. No. 11.	Thermometer in the liquid. No. 2.	Tensions.		Difference.
		Observed.	Calculated.	
°	°	mm	mm	mm
121·13	121·16	1530·27	1530·68	−0·41
121·13	121·16	1529·96	..	..
121·11	121·16	1529·18	..	..
123·91	123·90	1668·71	1668·88	−0·17
123·91	123·94	1670·34	..	..
123·91	123·94	1670·32	..	..
128·47	128·40	1915·12	1912·25	+2·87
128·47	128·38	1915·96	..	..
130·18	130·12	2012·51	2013·65	−1·14
130·20	130·15	2015·34	..	..
131·57	131·45	2097·93	2095·07	−2·86
131·57	131·45	2097·93	..	..
131·63	131·51	2098·28	..	..
133·32	133·21	2209·20	2207·00	+2·20
133·28	133·20	2209·08	..	..
136·09	135·92	2387·99	..	..
136·02	135·85	2386·07	2382·84	+3·23
136·00	135·83	2386·81	..	..
137·52	137·75	2514·79	..	..
137·54	137·77	2515·30	2520·10	−4·80
137·54	137·77	2515·30	..	..
137·54	137·77	2514·99	..	..
138·89	138·90	2599·23	2603·04	−3·81
138·89	138·90	2599·18	..	..
138·87	138·88	2597·97	..	..
138·82	138·84	2597·34	..	..
138·80	138·82	2596·43	..	..
138·75	138·66	2591·65	..	..
138·74	138·66	2591·65	..	..
138·74	138·65	2591·29	..	..
138·73	138·64	2590·61	..	..
141·59	141·61	2803·05	..	..
141·54	141·57	2799·68	..	..
141·56	141·58	2801·18	2808·82	−7·64
141·56	141·58	2801·77	..	..
141·56	141·59	2802·03	..	..
144·15	144·10	3010·19	..	..
144·17	144·12	3010·73	3015·93	−5·20
144·17	144·12	3009·44	..	..
145·98	145·88	3161·67	..	..
145·98	145·88	3161·63	3166·64	−5·01
145·98	145·88	3161·66	..	..
148·30	148·20	3360·74	..	..
148·30	148·20	3361·36	3374·53	−13·17
148·30	148·20	3361·36	..	..
148·30	148·24	3361·03	..	..
148·26	148·20	3359·54	..	..

* To obtain the calculated tensions in the series T., the temperatures given by the thermometer No. 11, which is one of those that were employed in the series R. and S., have been adopted. The thermometer No. 2 was subsequently broken by accident, on which account its indications could not be taken into account.

The next object is to calculate a formula of interpolation which shall represent all the observations in a satisfactory manner, and by means of which, we can determine the force of aqueous vapour corresponding to any given temperature.

A great number of different formulæ have been proposed to express the elastic force of aqueous vapour in functions of the temperature. Some of the formulæ were given as simple formulæ of interpolation, others were presented with greater pretensions, as really explanatory of the physical law of the phænomenon.

De Prony first proposed an expression of the form

$$e = a\alpha^t + b\beta^t + c\gamma^t + d\delta^t;$$

and he gave a general method for calculating, by means of observations, the values of the coefficients a, b, c, d, and the bases of the exponents α, β, γ, δ*.

Dr. Young proposed the formula adopted by many philosophers, $e = (a + bt)^m$.

MM. Dulong and Arago adopted an expression of the same form. The formula $e = (1 + 0{\cdot}7153\,t)^5$, calculated by these illustrious philosophers, contains only one constant quantity obtained from a single one of their observations, from that one made at the highest pressure.

Roche proposed the formula

$$e = a\,\alpha^{\frac{t}{m+nt}},$$

which he gives, not as a simple formula of interpolation, but as the mathematical expression of the phænomenon. The same formula has been since reintroduced by several natural philosophers, namely, by M. August†; it represents sufficiently well my own observations between the limits which served to calculate the constant quantities. I had occasion to settle that point in calculating the three constant quantities by means of the tensions at 0°, at 50°, and at 100°; but it is easy to see that it does not express the mathematical law of the phænomenon, and that it ought only to be considered as a formula of interpolation; the function is discontinuous, and represents a curve with two branches. In the case of $\alpha > 1$, one of these branches, which ought to represent the observed tensions, terminates where

* *Journal de l'Ecole Polytechnique*, 2e cahier, p. 1.

† Poggendorff's *Annalen*, vols. xiii. and lviii. The same formula has been adopted by M. Magnus in the paper mentioned in the Note to page 575.

$t = -\frac{m}{n}$, $e = 0$; the curve is then a tangent to the axis of the t: on leaving this point towards the positive t, the curve turns its convexity towards the axis of t, and presents a point of inflexion for $t = \frac{m(\log \alpha - 2n)}{2n^2}$; lastly, it is one of the asymptotes to the straight line $e = a\,\alpha^{\frac{1}{n}}$, parallel to the axis of the t. The other branch is one of the asymptotes to the same straight line $e = a\,\alpha^{\frac{1}{n}}$, and to the straight line $t = -\frac{m}{n}$, parallel to the axis of the e.

Lastly, M. Biot has given a new mode of interpolation*, which he has applied to the formation of a table of the elastic forces of aqueous vapour between $-20°$ and $220°$, trusting to the experiments of M. Gay-Lussac for temperatures below $100°$, and to the experiments of MM. Dulong and Arago for higher temperatures. The formula adopted by M. Biot is analogous to that of Prony; only that M. Biot makes the sum of the exponents equal the logarithm of the elastic force, and not the elastic force itself: he perceived that it could be confined to three terms, even supposing the base of one of the exponents to equal 1; so that he adopts the following formula,—

$$\log e = a + b\,\alpha^t + c\,\beta^t.$$

The five constant quantities which enter into this expression are determined by five observations conveniently distanced in the scale of temperatures. I have adopted M. Biot's mode of interpolation, which appears to me applicable with advantage to a large number of physical phænomena, and particularly to the relations which exist between the elastic forces of vapours and the temperatures.

I do not propose at present to calculate a formula which shall represent the phænomenon in its whole extent; the observations which I made at high pressures are not sufficiently complete, they ought to be carried much further: these observations present, besides, particular difficulties, which I shall presently point out, and which prevent me from regarding them as perfectly satisfactory. At present I shall only notice the elastic forces of aqueous vapour between $0°$ and $100°$. I determine the five constant quantities which enter the formula

$$\log e = a + b\,\alpha_1^t + c\,\beta_1^t$$

* *Comptes Rendus de l'Académie*, t. xii. p. 150.

by means of the elastic forces which correspond to the temperatures 0°, 25°, 50°, 75°, and 100°; letting A, B, C, D, E be their logarithms. Taking besides

$$(\alpha_1)^{25}=\alpha, \qquad \alpha_1=\sqrt[25]{\alpha},$$

whence

$$(\beta_1)^{25}=\beta; \qquad \beta_1=\sqrt[25]{\beta}.$$

We have then the five conditional equations,—

$$A = a + b + c, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$
$$B = a + b\alpha + c\beta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$
$$C = a + b\alpha^2 + c\beta^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$
$$D = a + b\alpha^3 + c\beta^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$
$$E = a + b\alpha^4 + c\beta^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

From the equations (1.), (2.), (3.), we obtain—

$$a = \frac{[A\alpha\beta-(\alpha+\beta)\,B+C]\,(\alpha-\beta)}{(\alpha-1)\,(\beta-1)\,(\alpha-\beta)},$$

$$b = \frac{[A\beta-(1+\beta)\,B+C]\,(\beta-1)}{(\alpha-1)\,(\beta-1)\,(\alpha-\beta)},$$

$$c = \frac{[-A\alpha+(1+\alpha)\,B-C]\,(\alpha-1)}{(\alpha-1)\,(\beta-1)\,(\alpha-\beta)}.$$

If the values are substituted in the equations (4.) and (5.), we obtain two equations containing only α and β.

Taking the equation (2.) from the equation (4.), we obtain

$$D-B = b\alpha\,(\alpha^2-1) + c\beta\,(\beta^2-1);$$

substituting for b and c their values, and reducing,

$$D-B = A\alpha\beta-B\,(\alpha+1)\,(\beta+1)+C\,(\alpha+\beta+1), \quad . \quad (6.)$$

or

$$D-C = (A-B)\alpha\beta-(B-C)\,(\alpha+\beta). \quad . \quad . \quad . \quad (7.)$$

Taking the equation (3) from the equation (5), we have

$$E-C = b\alpha^2\,(\alpha^2-1)+c\beta^2\,(\beta^2-1);$$

substituting for b and c their values, and reducing,

$$(\alpha+\beta)\,[A\alpha\beta-B(\alpha+1)(\beta+1)+C(\alpha+\beta+1)]+A\alpha\beta-C\alpha\beta=E-C;$$

or, in accordance with equation (6.),

$$(\alpha+\beta)\,(D-B)+(A-C)\,\alpha\beta=E-C. \quad . \quad . \quad . \quad . \quad (8.)$$

From the equation (6) and (8), are obtained

$$\alpha+\beta=\frac{(D-C)(A-C)-(E-C)(A-B)}{(A-C)\,(C-B)-(A-B)\,(A-C)},$$

$$\alpha\beta=\frac{(E-C)(C-B)-(A-C)(D-C)}{(A-C)(C-B)-(A-B)(A-C)},$$

from which are deduced α and β, and subsequently α_1 and β_1.

The values of the coefficients a, b, c are calculated afterwards by the formulæ

$$b=\frac{A\beta-(1+\beta)B+C}{(\alpha-\beta)(\alpha-1)},$$

$$c=\frac{-A\alpha+(1+\alpha)B-C}{(\alpha-\beta)(\beta-1)},$$

$$a=A-b-c.$$

A great number of determinations of the tension of aqueous vapour at 0° will be found in the preceding tables; but as perfect an accordance as I could have wished will not be met with in these determinations. It will be observed that the numbers obtained in the same series differ but very little; the errors of observation are therefore extremely small. The differences only become slightly perceptible when one series of experiments is compared with another; and in general when a difference is perceptible at 0° it remains constant at all higher temperatures; these differences therefore are attributable to constant errors, which I have in vain endeavoured to remove. I adopted in calculating the formula the number $4^{mm}\cdot60$ as the tension at 0°; it is the mean of the extreme observations 4·52 and 4·68.

The tensions corresponding to the temperatures 25°, 50° and 75°, were obtained by constructing with exactness, upon a large scale, the curve of the tensions, according to the results of the experiments, and correcting the numerical value of the ordinate taken upon the curve, by a little interpolation made upon the surrounding points, obtained directly from the observations. This interpolation did not sensibly change the values of the corresponding ordinates for $t = 25°$ and $t = 50°$. The graphic curve gave for $t = 75°$, $e = 288^{mm}\cdot8$; the interpolation reduced this value to $288^{mm}\cdot50$.

Setting out from the given numbers,

$t =$ 0°,	$e =$ 4·60 mm
$t =$ 25,	$e =$ 23·55
$t =$ 50,	$e =$ 91·98
$t =$ 75,	$e =$ 288·50
$t =$ 100,	$e =$ 760·00

we obtain

$$\left.\begin{aligned} \log \alpha_1 &= 0{\cdot}006865036, \\ \log \beta_1 &= \bar{1}{\cdot}9967249, \\ \log b &= \bar{2}{\cdot}1340339, \\ \log c &= -0{\cdot}6116485, \\ a &= +4{\cdot}7384380. \end{aligned}\right\} \quad \ldots\ldots \text{(A.)}$$

The tables show the accordance which exists between the results deduced from this formula, and those obtained by direct observation. I endeavoured to apply the same formula to temperatures below 0°, but I found that the elastic forces deduced from it were constantly higher than those established by observation. The difference is very small for the first negative degrees of the scale, but increases up to $0^{mm}{\cdot}25$ towards $-25°$; so that the curve deduced from the formula rises on leaving zero, and separates gradually from the curve observed for temperatures below 0°.

The same formula cannot therefore be employed for temperatures much below zero; I have calculated for these a little formula of interpolation,

$$e = a + b\,\alpha^x, \quad \ldots\ldots \text{(B.)}$$

in which $x = t - 32°$.

The three constant quantities were determined by the three following values:

$t = -32$,	$x = 0$,	$e = 0{\cdot}31$ mm;
$t = -16$,	$x = 16$,	$e = 1{\cdot}18$;
$t = 0$,	$x = 32$,	$e = 4{\cdot}60$.

In this manner was obtained

$$\left.\begin{aligned} \log b &= \bar{1}{\cdot}4724984, \\ \log \alpha &= 0{\cdot}0371566, \\ a &= +0{\cdot}0131765. \end{aligned}\right\} \quad \ldots\ldots \text{(B.)}$$

The temperatures were measured in all my experiments by a mercurial thermometer, which can be much more promptly and precisely read off than an air thermometer; but beyond 100° mercurial thermometers become inexact; they vary for the same temperature according to the nature of the glass of which the reservoir is constructed, and probably according to the manner in which the reservoir has been blown. The four thermometers which were employed in my experiments below 100°, were constructed with tubes of crystal all coming from the same

melting; the reservoirs were blown upon the stems by the same workmen, and nevertheless these thermometers did not present so complete an accordance in their indications as might reasonably have been expected, from the extreme care with which the divisions had been made and their scales tested. This obstacle is overcome by observing the temperatures above 100° directly by an air thermometer; but to render this latter instrument susceptible of a certain amount of exactitude, it ought to be of considerable size, in order that the tubes, in which the changes of the elastic force of air are measured, may have so large a bore, as to affect but insensibly the height of the liquid contained in them by capillary action. But such an instrument could not be placed in my apparatus. I preferred therefore to observe in a direct manner the temperatures on mercurial thermometers, and to compare afterwards these same thermometers with an air thermometer constructed in the proper manner, and placed in similar circumstances to those, in which these instruments are placed in my retort. I have already made several attempts to make this comparison, but the results are not satisfactory; I propose therefore to make fresh experiments and to publish them with the remainder of my observations on the elastic force of aqueous vapour at high temperatures.

In the mean time I thought it better to connect the observations made up to this time for high temperatures by a provisional formula of interpolation, which enables us easily to study their course. I adopted simply the formula with two terms,

$$\log e = a + b\alpha^x.$$

The three constant quantities in this formula were calculated by the following values,

$t = 100°$	$e = 760{\cdot}0^{mm}$;
$t = 123$	$e = 1621{\cdot}0$;
$t = 146$	$e = 3177{\cdot}0$;

which were taken on the graphic curve constructed from the observations of the series R.

Thus is obtained

$$\left.\begin{array}{rl} \log \alpha = & \bar{1}{\cdot}9977641 \\ \log b = & 0{\cdot}4692291 \\ a = & +\,5{\cdot}8267890 \end{array}\right\} \quad \ldots\ldots \quad (C.)$$

The formula is

$$\log e = a - b\alpha^x, \qquad x = t - 100°. \quad \ldots\ldots \quad (C.)$$

The tables show that this formula represents the observations pretty well; the greatest difference amounts to $13^{mm}\cdot2$; and corresponds to an error in the valuation of the temperature of $0^{\circ}\cdot15$.

The experiments published in this memoir are therefore represented by three partial formulæ of interpolation, the object of which is, to enable us to study the course of the observations. When I shall have completed my experiments at high temperatures, and compared the mercurial thermometers used in these experiments with an air thermometer, I intend to ascertain, whether it is possible to represent the whole of the observations by a single formula.

At the end of this memoir will be found the Table of the elastic force of aqueous vapour calculated from the formulæ A and B for all degrees of temperature comprised between -32° and 100°.

Very precise determinations of the elastic force of aqueous vapour for temperatures somewhat below 100° may be obtained, by observing the temperature at which water boils at different stations in ascending a high mountain. MM. Bravais and Peltier, at my request, made some observations of this nature on ascending the Faulhorn, during the summer of 1842. The note containing the details of these experiments is published in the *Comptes Rendus de l'Académie*, tome xviii. page 572.

The numbers obtained by MM. Bravais and Peltier differ considerably from those deduced from my observations. It must be mentioned, that the thermometer used by those gentlemen was very irregular in its indications at the zero point; similar irregularities were consequently observable at the boiling-points.

Another series of experiments was made by M. Marié, Professor of Natural Philosophy at the College of St. Etienne, in December 1843, in ascending Mont Pila. The details of these experiments were published in the *Comptes Rendus de l'Académie*, tome xviii. page 252.

I shall confine myself here to transcribing the results, and shall exhibit the elastic forces calculated for the same temperatures by means of my formula.

Temperature at which the water boils.	Elastic force.		Difference.
	Observed.	Calculated.	
°	mm	mm	mm
99·87	756·69	756·59	+0·10
99·40	745·06	743·94	+1·12
98·61	723·52	723·06	+0·46
98·36	716·45	716·56	−0·11
97·70	700·30	699·63	+0·67
96·80	679·63	677·07	+2·56
96·38	666·94	666·75	+0·19
95·95	655·79	656·33	−0·54
95·49	645·99	645·33	+0·66

The observations of M. Marié therefore accord with the formula as much as could be desired.

Table of Elastic Forces of Aqueous Vapour from − 32° *to* ~~100~~.

Temperatures in centigrade degrees.	Elastic forces in millimetres of mercury.	Difference.	Temperatures in centigrade degrees.	Elastic forces in millimetres of mercury.	Difference.
°	mm	mm	°	mm	mm
−32	0·310	0·026	−16	1·179	0·105
31	0·336	0·029	15	1·284	0·114
30	0·365	0·032	14	1·398	0·123
29	0·397	0·034	13	1·521	0·135
28	0·431	0·037	12	1·656	0·147
27	0·468	0·041	11	1·803	0·160
26	0·509	0·044	10	1·963	0·174
25	0·553	0·049	9	2·137	0·190
24	0·602	0·052	8	2·327	0·206
23	0·654	0·057	7	2·533	0·225
22	0·711	0·063	6	2·758	0·246
21	0·774	0·067	5	3·004	0·267
20	0·841	0·075	4	3·271	0·282
19	0·916	0·080	3	3·553	0·326
18	0·996	0·088	2	3·879	0·345
17	1·084	0·095	1	4·224	
16	1·179				

Table of Elastic Forces of Aqueous Vapour from 0° *to* 100°.

Temperatures.	Elastic forces.	Difference.	Temperatures.	Elastic forces.	Difference.
°	mm	mm	°	mm	mm
0	4·600	0·340	50	91·982	4·679
1	4·940	0·362	51	96·661	4·882
2	5·302	0·385	52	101·543	5·093
3	5·687	0·410	53	106·636	5·309
4	6·097	0·437	54	111·945	5·533
5	6·534	0·464	55	117·478	5·766
6	6·998	0·494	56	123·244	6·007
7	7·492	0·525	57	129·251	6·254
8	8·017	0·557	58	135·505	6·510
9	8·574	0·591	59	142·015	6·776
10	9·165	0·627	60	148·791	7·048
11	9·792	0·665	61	155·839	7·331
12	10·457	0·705	62	163·170	7·621
13	11·162	0·746	63	170·791	7·923
14	11·908	0·791	64	178·714	8·231
15	12·699	0·837	65	186·945	8·551
16	13·536	0·885	66	195·496	8·880
17	14·421	0·936	67	204·376	9·220
18	15·357	0·989	68	213·596	9·569
19	16·346	1·045	69	223·165	9·928
20	17·391	1·104	70	233·093	10·300
21	18·495	1·164	71	243·393	10·680
22	19·659	1·229	72	254·073	11·074
23	20·888	1·296	73	265·147	11·477
24	22·184	1·366	74	276·624	11·893
25	23·550	1·438	75	288·517	12·321
26	24·988	1·517	76	300·838	12·762
27	26·505	1·596	77	313·600	13·211
28	28·101	1·681	78	326·811	13·677
29	29·782	1·766	79	340·488	14·155
30	31·548	1·858	80	354·643	14·644
31	33·406	1·953	81	369·287	15·148
32	35·359	2·052	82	384·435	15·666
33	37·411	2·154	83	400·101	16·197
34	39·565	2·262	84	416·298	16·743
35	41·827	2·374	85	433·041	17·303
36	44·201	2·490	86	450·344	17·877
37	46·691	2·611	87	468·221	18·466
38	49·302	2·737	88	486·687	19·072
39	52·039	2·867	89	505·759	19·691
40	54·906	3·004	90	525·450	20·328
41	57·910	3·145	91	545·778	20·979
42	61·055	3·291	92	566·757	21·649
43	64·346	3·444	93	588·406	22·334
44	67·790	3·601	94	610·740	23·038
45	71·391	3·767	95	633·778	23·757
46	75·158	3·935	96	657·535	24·494
47	79·093	4·111	97	682·029	25·251
48	83·204	4·295	98	707·280	26·025
49	87·499	4·483	99	733·305	26·695
50	91·982		100	760·000	

Article XXI.

Hygrometrical Researches. *By* M. V. Regnault.

[From the *Comptes Rendus*, T. xx. pp. 1127 and 1220 for April 1845.]

THE general problem of hygrometry consists in determining the quantity of aqueous vapour existing at any time in a given volume of air, and the relation between this quantity and that which the air would contain if it were perfectly saturated. The different methods which have been proposed to attain this object are of two kinds.

The first are purely chemical: they consist in absorbing, by means of substances which have a great affinity for water, the vapour contained in a certain volume of air, and in determining its weight by the balance. The others are founded on the observation of certain physical phænomena, such as the greater or lesser elongation which substances of organic origin experience in air more or less near to the state of saturation, or on the determination of the temperature to which the air must be lowered in order to be saturated by the quantity of humidity which it holds.

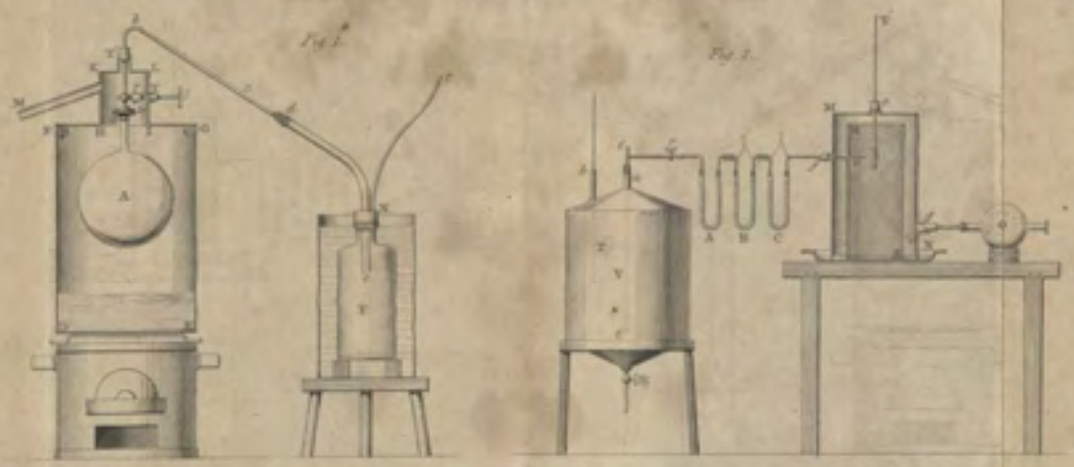
All these methods presuppose the exact knowledge of certain physical laws and of several numerical data, as—

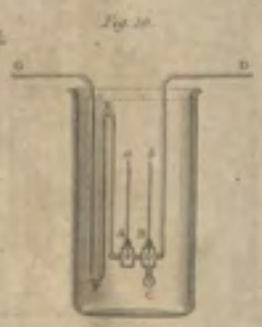
1. An exact table of the elastic forces of aqueous vapour *in saturated air* for all atmospherical temperatures;

2. The density of the aqueous vapour in relation to the air taken under the same circumstances, when *the air is saturated with the vapour*;

3. The density of this same vapour when the air is saturated in a greater or less degree with it.

The memoir which I have the honour to lay before the Academy contains the results of numerous experiments in which I have been engaged for several years, on that branch of general physics, which, notwithstanding the efforts of several distinguished philosophers, still presents many points of uncertainty. I shall divide this investigation into two parts: in the first, I shall direct my attention to the fundamental data which I have just enumerated; and the second part will be devoted to the examination of the hygrometrical processes.





Scale of Figs. 1, 2 & 3. 1 metre.

Scale of Figs. 4, 5 & 10. 1 metre.

Scale of Figs. 6, 7, 8 & 9. 1 metre.

Regnault's Hygrometrical Researches

Part I.

Of the Elastic Forces of Aqueous Vapour in the Air.

The maximum elastic forces of aqueous vapour *in vacuo* have been determined by a great number of experimenters; but the results of their experiments differ far too much to establish the law of the elastic force of aqueous vapour *in vacuo* with any degree of certainty. I have myself lately made a great number of experiments on this subject by various methods, and, I believe, with all the means of precision which science at present offers. As the results which have been obtained have always agreed, I am certainly justified in regarding the table calculated from these experiments as preferable to all those which have been published previously, and in the following pages I shall adopt it exclusively for the calculation of the maximum elastic forces of aqueous vapour *in vacuo*.

In hygrometrical observations, we require to know the elastic force of aqueous vapour, not *in vacuo*, but in the air under the pressure of the atmosphere. It is admitted that these elastic forces are absolutely the same as those which exist *in vacuo*. I have in vain sought in the annals of science the experiments by which this identity has been established, and I do not think that by means of the apparatus which are described in the elementary treatises on Physics we can institute experiments sufficiently precise to leave no doubt on this subject.

It appeared to me necessary to make some new experiments to decide this delicate question, employing apparatus exactly similar to those which I used to determine the tensions of aqueous vapour *in vacuo*, in order that the results of the two series of experiments should allow of more strict comparison.

The tensions of aqueous vapour in saturated air may be determined by means of the apparatus described in my memoir 'On the Elastic Force of Aqueous Vapour'. Only the apparatus consisting of the two barometers is replaced by a system of two communicating tubes, arranged as in fig. 8, Pl. VII., and care is taken in each experiment to restore the level of the mercury to one and the same line, marked on the tube $p\,q$, in order that the volume of air may always remain the same, and that its elastic force alone may vary.

A small glass bulb, filled with water and sealed, is previously placed in the balloon. The balloon is perfectly dried, and finally

filled with dry air under the pressure of the atmosphere, whilst the balloon is surrounded by melting ice. The mercury is brought exactly to the line of level on the tube *p q*, whilst the balloon still communicates freely with the air; lastly, the tube *lf*, fig. 1, is sealed over the lamp. The ice surrounding the balloon is removed, and the vessel VV' filled with water, which is successively raised to higher temperatures. At each observation the mercury is restored to the mark on the tube *p q*, the water of the vessel is kept at a stationary temperature, as stated in the preceding memoir, page 565, the difference of height in the two columns of mercury is determined, and the barometer noted. The apparatus thus acts as an air thermometer, and it is ascertained that its indications correspond exactly with those of the mercurial thermometer immersed in the same water.

The water is then removed from the vessel, the bulb broken by bringing some incandescent charcoal near to the bottom of the balloon, the water replaced in the vessel, and the same series of observations recommenced on the air saturated with humidity which had been previously made on dry air. The difference of the elastic forces found in the two cases, and corresponding with the same temperature, is evidently equal to the tension of the aqueous vapour saturating the air at the same temperature.

The tension of the aqueous vapour in the air cannot be determined with the same precision as *in vacuo*; it requires greater precaution, and the error committed relative to the expansion of the air is added to that which occurs for the elastic force. Moreover, the maximum tension of the vapour occurs instantaneously *in vacuo*, whereas it requires a somewhat long time to be established in the air. It is necessary to ascertain with certainty, by observations repeated at distant intervals, and for one and the same stationary temperature, whether the tension does not continue to increase.

For greater certainty, a first series of experiments was made, by raising successively the temperature of the water of the vessel, so that the air had to dissolve a further quantity of vapour; a second series was then made, in which, on the contrary, the temperature of the water was gradually lowered; the air then deposited a portion of the water which it had previously held in solution. The elastic forces of the vapour at the same temperature should be found identical in these two series.

The following tables contain the results obtained by this me-

thod. The weight of the water which filled the bulb was about 1·5 grm. It was distilled water which had not been boiled; consequently it contained the quantity of air which it can dissolve at the ordinary temperature.

The second column of the table contains the tensions observed in the air; the third, the elastic forces of the aqueous vapour *in vacuo*, calculated for the same temperatures by means of the Table given in page 605.

TABLE I.—*Tensions of the Vapour of Water in Air.*

Temperatures. Centig.	Tensions of the vapour observed in air.	Tensions calculated by the formula.	Differences.	Temperatures. Centig.	Tensions of the vapour observed in air.	Tensions calculated by the formula.	Differences.
°	mm	mm	mm	°	mm	mm	mm
0·00	4·47	4·60	−0·13	31·00	32·97	33·41	−0·44
12·48	10·08	10·77	−0·69	31·00	33·16	33·41	−0·25
12·59	10·31	10·85	−0·54	34·25	39·98	40·13	−0·15
14·57	11·83	12·36	−0·53	18·26	15·06	15·61	−0·55
14·60	11·91	12·39	−0·48	18·22	15·04	15·57	−0·53
15·00	12·38	12·70	−0·32	22·12	19·07	19·81	−0·74
15·05	12·46	12·74	−0·28	22·15	19·15	19·84	−0·69
18·24	15·32	15·59	−0·27	25·72	24·14	24·59	−0·45
18·23	15·48	15·58	−0·10	25·74	24·05	24·62	−0·57
21·07	18·28	18·58	−0·30	29·28	29·66	30·28	−0·62
21·00	18·27	18·49	−0·22	29·32	29·79	30·35	−0·56
23·15	20·74	21·08	−0·34	32·80	36·45	37·00	−0·55
23·10	20·77	21·02	−0·25	32·78	36·39	36·96	−0·57
24·69	22·70	23·13	−0·43	35·97	43·39	44·13	−0·74
24·69	22·73	23·13	−0·40	35·95	43·48	44·08	−0·60
27·88	27·59	27·91	−0·32	37·96	48·70	49·20	−0·50
27·91	27·65	27·96	−0·31	38·00	48·70	49·30	−0·60

TABLE II.—*Tensions of the Aqueous Vapour in Nitrogen.*

Temperatures. Centig.	Elastic force of the vapour observed in nitrogen.	Elastic force of the vapour calculated by the formula.	Differences.	Temperatures. Centig.	Elastic force of the vapour observed in nitrogen.	Elastic force of the vapour calculated by the formula.	Differences.
°	mm	mm	mm	°	mm	mm	mm
0·00	4·31	4·60	−0·29	5·27	5·99	6·66	−0·67
0·00	4·43	4·60	−0·17	5·27	5·96	6·66	−0·70
0·00	4·44	4·60	−0·16	13·12	10·58	11·25	−0·67
16·49	13·29	13·96	−0·67	13·16	10·67	11·30	−0·63
16·50	13·36	13·98	−0·62	17·19	14·07	14·60	−0·53
15·71	12·64	13·29	−0·65	17·19	14·07	14·60	−0·53
15·75	12·72	13·33	−0·61	21·46	18·65	19·03	−0·38
12·87	10·26	11·07	−0·81	21·46	18·61	19·03	−0·42
12·89	10·35	11·08	−0·73	25·50	23·71	24·27	−0·56
10·90	9·14	9·73	−0·59	25·52	23·71	24·31	−0·60
10·99	9·19	9·78	−0·59	28·92	28·96	29·65	−0·69
8·56	7·67	8·33	−0·66	28·90	28·81	29·61	−0·80
8·59	7·74	8·34	−0·60	32·50	35·92	36·38	−0·46
7·54	7·06	7·77	−0·71	32·53	36·01	36·45	−0·44
7·59	7·17	7·79	−0·62				

TABLE III.—*Tensions of Aqueous Vapour in Nitrogen Gas.*

Temperatures. Centig.	Tensions of the vapour observed in nitrogen gas.	Tensions of the vapour calculated by the formula.	Differences.	Temperatures. Centig.	Tensions of the vapour observed in nitrogen gas.	Tensions of the vapour calculated by the formula.	Differences.
	mm	mm	mm		mm	mm	mm
18·91	15·97	16·26	−0·29	29·56	30·15	30·77	−0·62
18·95	16·03	16·30	−0·27	29·58	30·16	30·81	−0·65
15·90	12·69	13·45	−0·76	31·88	34·51	35·16	−0·65
15·92	12·75	13·47	−0·72	31·90	34·53	35·21	−0·68
20·00	16·78	17·39	−0·61	34·30	39·58	40·24	−0·66
19·98	16·72	17·37	−0·65	34·32	39·54	40·28	−0·74
21·80	18·71	19·43	−0·72	37·75	47·67	48·65	−0·98
21·79	18·72	19·42	−0·70	37·77	47·73	48·70	−0·97
23·88	21·34	22·03	−0·69	37·74	47·80	48·63	−0·83
23·90	21·33	22·06	−0·73	39·81	53·63	54·36	−0·73
25·44	23·41	24·18	−0·77	39·81	53·70	54·36	−0·66
25·44	23·47	24·18	−0·71	39·81	53·72	54·36	−0·64
26·96	25·63	26·44	−0·81	31·00	32·68	33·41	−0·73
26·97	25·76	26·44	−0·68	30·99	32·66	33·39	−0·73

The first series of experiments was made in air; it is seen by Table I. that the tensions of the aqueous vapour in air are constantly weaker than those which are obtained *in vacuo*.

I feared that this circumstance was produced by the absorption of a small portion of the oxygen of the air by the mercury, experience having shown that, in moist and rather warm air, mercury is rapidly oxidized on its surface. To obviate this presumed cause of error, I made two other series of experiments, filling the balloon with nitrogen, but the results were still the same, as may be seen in Tables II. and III.

It would appear to result from this that the tension of the aqueous vapour in the air is rather weaker than that which exists for the same temperature *in vacuo*; but the difference is very small, and it may perhaps be attributed to a constant error in the process. My efforts to determine the cause of such an error have led to no result.

I propose to determine with the greatest care the elastic forces of the vapour of æther *in vacuo* and in air. As these elastic forces are much more considerable at the temperatures of the atmosphere than those of aqueous vapour, we may hope to ascertain more easily whether the tensions are identical or different in the two cases.

Meanwhile we admit, in the calculations which we shall have to make of the fractions of saturation of the air, the elastic forces inserted in the table which I have cited, and which gives the tensions *in vacuo*. It will be easy to make subsequently the re-

quisite correction, if it be found that these tensions are really somewhat greater than those which exist in the air.

Of the Density of Aqueous Vapour.

What are the densities of aqueous vapour *in vacuo* and in the air, at the state of saturation or of non-saturation, for different temperatures and under different pressures?

It is generally admitted that it is sufficient to determine by direct experiment the density of aqueous vapour for one temperature and pressure, and that the densities of this vapour may be subsequently calculated for all the other temperatures and pressures, by applying Mariotte's law, and that of the uniform dilatation of gases. Now, experiment has shown that these laws are not verified, in most gases, even when these are far removed from their point of liquefaction. Consequently it is to be feared that these laws are not perfectly accurate for aqueous vapour, especially at the state of saturation, that is to say, at the very point of its liquefaction.

A theoretical value of the density of aqueous vapour may be obtained by applying to this substance M. Gay-Lussac's law on the composition of gases.

Thus, 2 volumes of hydrogen weigh . .	0·1382
1 volume of oxygen weighs . . .	1·1055
2 volumes of aqueous vapour . .	1·2437

Hence the theoretical density of aqueous vapour is 0·6219.

Now it is necessary to ascertain whether the densities of aqueous vapour under these different circumstances may be deduced by calculation from this theoretical density. It is impossible to decide this question with the means which science at present possesses. We have, in fact, a great number of determinations of the density of aqueous vapour, made under the most varied circumstances by a great number of experimenters; but they present such extraordinary discrepancies, that it is impossible to ascertain the truth. They may be judged of by the following citations*:—

Watt	100·00	0·6334
Davy	Mean.	0·6666
Dalton	Id.	0·7000
Saussure	5·94	0·7409

* These quotations are extracted from the memoir of M. Schmedding, which wil be considered hereafter.

Saussure	7°·73	0·6858
Id.	18·95	0·6833
Clement and Desormes	12·50	0·5311
Id.	12·50	0·5471
Anderson	9·45	0·6523
Id.	15·00	0·6630
Id.	25·00	0·6324
Id.	28·34	0·6251
Mayer	18·75	0·8012
Despretz	17·44	0·6767
Id.	19·31	0·6535
Gay-Lussac . . .	100·00	0·6235
Brunner	9·50	0·6490
Schmidt	100·00	0·7220
Southern	109·45	0·6479
Id.	132·23	0·6957
Id.	146·13	0·7095
Muncke	0·00	0·8274
Id.	3·75	0·8469
Id.	7·50	0·8836
Id.	8·44	0·8892
Id.	9·38	0·9076
Id.	12·50	0·8662
Id.	15·00	0·7957
Id.	18·75	0·7186
Id.	20·00	0·6594
Id.	22·50	0·6940
Id.	23·75	0·7214
Id.	24·37	0·7335
Id.	27·50	0·7335
Id.	37·50	0·6501
Id.	43·75	0·6348

It is evident that the majority of these results are wholly incorrect; and it is sufficient to peruse the processes followed by the authors, to perceive immediately that the results obtained by most of them are not the least to be depended upon.

The density of vapour proposed by M. Gay-Lussac, $\frac{5}{8}$, has been generally adopted. This density differs little from the theoretical density; and it need only be remarked, that it was not determined on vapour in the state of saturation, but on vapour at 100° under a weaker pressure than that of $0^{m}{\cdot}760$.

A German philosopher, M. Schmedding, published some years ago in Poggendorff's *Annalen* (vol. xxvii. p. 40), an extensive and carefully executed research, in which he determined the weight of aqueous vapour in air in the state of saturation at different atmospheric temperatures; and he arrived at the result, that the density of aqueous vapour in the saturated air in relation to that of air taken under the same circumstances, increases in a very striking manner with the temperature. This variation may be judged of by the following numbers extracted from his memoir:—

13°·44	0·616
16·25	0·621
17·50	0·625
18·75	0·627
20·00	0·630
21·25	0·632
22·50	0·634
23·75	0·643
28·75	0·643
37·50	0·640
43·75	0·652

The density of aqueous vapour varies therefore from 0·616 to 0·652 between the temperatures of 13° C. and 44° C. We should therefore commit considerable errors by calculating the weight of the vapour which should be in a state of saturation in a cubic metre of air, with the theoretical density of which I have just spoken, and by applying Mariotte's law and that of the uniform dilatation of the gases.

I have made several experiments to decide this point, which is the basis of the theory of hygrometry.

I first determined the density of aqueous vapour *in vacuo*, at the temperature of 100°, but under progressively decreasing pressures, in order to ascertain whether the vapour followed in this case the law of Mariotte. The apparatus which I employed consists of a balloon A (Plate VIII. fig. 1) of about 10 litres capacity, bearing a brass mounting with a stopcock *r*. This mounting is fixed to the neck of the balloon by means of red-lead cement, in the manner which I have described in my memoir on the density of gases*; it terminates in a curved brass tube.

* *Comptes Rendus*, vol. xx. p. 975.

A small quantity of water is introduced into the balloon, which is then put in communication with an air-pump; a tube containing pumice-stone moistened with sulphuric acid is interposed to prevent the aqueous vapour from penetrating into the parts of the air-pump. A vacuum is formed for a considerable length of time. The vapour which is incessantly produced in the balloon finally expels the whole of the air, upon which the stopcock is closed. The balloon is placed in a large vessel of galvanized sheet-iron B C D E, so that the stopcock r is in front of a tubulature T fitted to the vessel. This vessel, which contains a layer of water two decimetres thick, is heated over a furnace. The extremity of the tube $b\,c$ is inserted in a brass tube $c\,d$ which is itself soldered to a flexible leaden tube $d\,e$ forming part of the mounting N of a large flask F. The flask F is kept in the water at the ambient temperature. A small leaden tube t forms a communication between the flask F and a barometrical manometer.

A partial vacuum is formed in the flask F, and when the water is in full ebullition in the vessel B C D E, the stopcock r is opened. The water of the balloon then distils over, and condenses in the flask F. At the end of about an hour the elastic force of the vapour is measured on the barometric manometer, and the stopcock r is closed. The communicating tube $b\,c$ is completely dried, and the balloon is weighed after having been left till the following day on the hook of the scales. In this weighing, likewise, the method is followed which I have described in my memoir on the determination of the density of gases *.

The balloon is arranged anew in the vessel B C D E, placing it in communication with the flask F. The water is raised to the boiling-point and an almost perfect vacuum is formed. On opening the stopcock r, the greatest part of the vapour contained in the balloon condenses in the flask F, and there only remains a very small quantity, which holds in equilibrium the elastic force remaining in the flask F. This is carefully measured when the equilibrium is established, and the stopcock r is closed.

The balloon is weighed. The difference p of the two weights is the weight of the vapour which fills the balloon at the temperature T of boiling water under a pressure equal to the difference h of the elastic forces observed in the two experiments.

The weight π of the dry air which fills the balloon at 0°, under

* *Annales de Chimie et de Physique*, 3ième Série, vol. xiv. p. 211.

the pressure of 760 millimetres, was determined by direct experiments.

The density δ of the vapour with relation to the air taken under the same circumstances of temperature and pressure will be expressed by the formula

$$\delta = \frac{p}{\pi} \cdot \frac{1 + \alpha T}{1 + k T} \cdot \frac{760}{h}.$$

The following are some numbers obtained in this manner:—

$$\left.\begin{aligned} \pi &= 12^{\text{grms}}\cdot 9937 \\ p &= 2^{\text{grms}}\cdot 959 \\ h_0 &= 378^{\text{mm}}\cdot 72 \\ T &= 99°\cdot 91. \end{aligned}\right\} \quad \ldots\ldots \quad \text{(I.)}$$

Weight of the vapour at 0°, and under a pressure of 760^{mm},

$$P = 8^{\text{grms}}\cdot 0965.$$

$$\left.\begin{aligned} p &= 2^{\text{grms}}\cdot 802 \\ h_0 &= 357^{\text{mm}}\cdot 51 \\ T &= 99°\cdot 14 \\ P &= 8^{\text{grms}}\cdot 1052. \end{aligned}\right\} \quad \ldots\ldots \quad \text{(II.)}$$

$$\left.\begin{aligned} p &= 1^{\text{grm}}\cdot 261 \\ h_0 &= 161^{\text{mm}}\cdot 32 \\ T &= 99°\cdot 63 \\ P &= 8^{\text{grms}}\cdot 0941. \end{aligned}\right\} \quad \ldots\ldots \quad \text{(III.)}$$

$$\left.\begin{aligned} p &= 2^{\text{grms}}\cdot 696 \\ h_0 &= 345^{\text{mm}}\cdot 28 \\ T &= 99°\cdot 78 \\ P &= 8^{\text{grms}}\cdot 0859. \end{aligned}\right\} \quad \ldots\ldots \quad \text{(IV.)}$$

We deduce from these four experiments,—

	Weight of vapour.	Density.
I. . . .	8·0965 grms.	0·62311
II. . . .	8·1052 ...	0·62377
III. . . .	8·0941 ...	0·62292
IV. . . .	8·0859 ...	0·62229

These densities differ little from the theoretical density 0·622, and from the density $\frac{10}{16}$ given by M. Gay-Lussac.

By applying the same method to the determination of the density of aqueous vapour taken under pressures approaching 760 millimetres, we obtain perceptibly higher numbers. This may result from the vapour being, in this case, at a tempera-

ture very near that at which saturation would occur; but it may equally arise from the glass of the balloon retaining condensed water on its surface by virtue of its hygroscopic property. When, on the contrary, this method is employed in the determination of the density of aqueous vapour under very weak pressures, the least errors in the weighings cause much more considerable ones in the numerical value of the density. Moreover this method does not admit of obtaining the density of the vapour at other temperatures than 100°; it is important to determine this density at temperatures more and more approaching that which would produce saturation.

The following process admits of these new determinations being made with greater precision. A large glass balloon is gauged exactly by weighing it full of water. Into this balloon a small glass bulb is introduced hermetically closed, and containing a quantity of water accurately weighed. The neck of this balloon is cemented into a tubulature which establishes the communication with a barometrical manometer. The balloon, as well as the manometer, is arranged in a large vessel filled with water. By means of a piece of plate glass the manometer may be measured by the cathetometer. All the precautions are moreover taken which have been described at length in my memoir on the elastic force of aqueous vapour*.

The balloon is dried, as complete a vacuum as possible is then formed, and the elastic force of the small quantity of air which remained in the balloon is then measured very exactly. By means of a piece of incandescent charcoal the glass bulb is broken, and the temperature of the water which surrounds the balloon is raised above that at which the vapour would be in a state of saturation. This temperature is rendered stationary, and the elastic force which exists in the balloon is measured. On subtracting from this elastic force that which belongs to the air, we obtain the elastic force of the vapour.

Whilst the temperature is lower than that at which the space would be saturated by the weight p of water contained originally in the glass bulb, we shall find, for the tension of the vapour, the maximum tension which corresponds to that temperature; but beyond that temperature the vapour will behave like a gas, and designating its elastic force by f, we shall have for its density relative to that of the air taken under the same

* See preceeding Memoir, p. 570.

circumstances of temperature and pressure,

$$\delta = \frac{p}{\pi} \cdot \frac{1 + \alpha T}{1 + kT} \cdot \frac{760}{f}.$$

I have only made a single series of experiments by this method, and an accident prevented my obtaining good results. I purpose shortly to resume these determinations.

The same apparatus may serve to determine the density of aqueous vapour in the air taken under different pressures: in this case an ordinary manometer is substituted for the barometrical manometer. But the determinations unfortunately in this case no longer present the same precision as *in vacuo*, and this for reasons which I have stated above (page 608), when our attention was directed to the determination of the tensions of aqueous vapour in the air.

Let us now direct our attention to the determination of the density of aqueous vapour *in the air in a state of saturation.* We have seen above that this question has been treated of by M. Schmedding, who found that the density of the vapour increased in this case rapidly with the temperature.

I determined the density of aqueous vapour in a state of saturation in the air, by weighing the quantity of humidity which a known volume of saturated air contains at different temperatures. For this purpose I employed the process of M. Brunner, which consists in filling a vessel of known capacity with water, making the upper part of this vessel communicate with tubes containing drying substances and which have been exactly weighed, and causing the water of the vessel to run off in a regular manner by an inferior orifice; the water which runs off below is replaced, in the upper part, by an equal volume of air. The aspirated air is completely deprived of its humidity in passing through the tubes. When the aspirator is emptied of water, the tubes are weighed; their increase in weight represents the weight of the water which existed in a volume of air equal to the capacity of the aspirator.

A similar process was employed by M. Schmedding; but I found that, to obtain accurate results, certain precautions must be taken.

The aspirator which I have used is formed of a cylindrical vessel of galvanized sheet-iron, terminated by two conical ends. The upper end has two tubulatures: the central one *a*, in which

a tube tt' is hermetically fixed, which acts as a Mariotte's tube to render the current constant; in the second tubulature b, a thermometer T is fitted, the bulb of which occupies the centre of the vessel. The lower end has a single tubulature with a graduated stopcock R, which has a tube 1 decimetre long, which remains filled with water when the current ceases, and prevents the external air from entering the lower tubulature when the vessel is emptied.

The tube of Mariotte has a stopcock r, which allows of stopping the aspiration of the air, and a U-shaped tube filled with pumice-stone moistened with sulphuric acid, which remains constantly fixed to the apparatus. The object of this tube is to prevent the vapour passing from the aspirator to the counterpoised drying tubes B and C.

To absorb the humidity of the air, I only employed two U-shaped tubes, $0^m{\cdot}18$ in height, and filled with coarse fragments of pumice-stone moistened with sulphuric acid: fine fragments would oppose too much resistance to the passage of the gas, and the air in the aspirator would no longer present the same elastic force as the external air.

The two tubes intended to absorb completely the humidity of the air are very short; I have endeavoured to make them as small as possible, because I attach great importance to rendering this method eminently practical and easy of execution in all hygrometric experiments. Experiment demonstrates moreover that these two tubes completely retain the humidity of the air. The first tube generally absorbs the whole of the water, and it is rare that the second tube gains 1 or 2 milligrammes in weight. I did not however regard this proof as sufficient. I wished to ascertain whether, on putting at the end of these two first tubes several others filled with pumice-stone moistened with sulphuric acid and immersed in refrigerating mixtures, these latter tubes would not increase in weight. I attached to the end of the second counterpoised tube a third tube which had been immersed in ice, then a fourth, which was placed in a refrigerating mixture of ice and chloride of calcium, at a temperature of -30 degrees.

The experiment was made in the usual way; the tubes 3 and 4 were afterwards placed under a bell-glass with some quick lime, where they were left for several hours, that they might exactly take the temperature of the ambient air. It was found that they presented exactly the same weight as before the expe-

riment. The tube No. 1 had absorbed 1·235 grm. of water; the tube No. 2 had not absorbed any. Thus the first tube had completely dried the air.

I made a second experiment, which will appear more conclusive than the last. Before the counterpoised tube, No. 1, I attached a tube filled with moistened sponge, and in front of this latter tube, three U-shaped tubes, filled with pumice-stone moistened with sulphuric acid, each 1 metre long; the third of these large tubes was immersed in a mixture of ice and chloride of calcium; the air consequently arrived perfectly dry in the tube containing the wet sponge; there it took up a fresh quantity of moisture, which it deposited in the drying counterpoised tubes.

The tube with wet sponge lost in this experiment .	0·767 gr.
The drying-tube, No. 1, gained	0·767
The tube, No. 2, gained	0

These experiments prove most evidently that the first drying-tube suffices, notwithstanding its small dimensions, to dry the air completely. The tube No. 2 is only confirmatory, and as such it is well to preserve it.

I may observe in passing, that by multiplying the apparatus intended to absorb gases or vapours, in the hope of obtaining a more complete absorption, much greater errors are committed in the weighings than those which it is sought to avoid. In fact, when the volume of the absorbing apparatus is considerable, we cannot neglect in the weighings the changes which supervene in the nature of the external air during the interval between the two weighings. Now, these changes cannot be determined with any precision. The least difference between the temperature of the external air and that of the apparatus at the moment of weighing,—a difference which it is impossible to avoid,—occasions a perceptible error. Lastly, the vitreous, eminently hygroscopic surface of the apparatus may be covered with an unequal quantity of humidity in the two weighings.

In experiments which require great accuracy, the experimenter should seek to reduce the apparatus to the smallest possible dimensions, instead of increasing them, as there is at the present day a tendency to do. The multiplication of the apparatus causes moreover too great resistances to the passage of the gas, and it becomes impossible to answer for the equality of pressure in the different parts of the apparatus.

In order to obtain a current of air saturated with moisture at a fixed temperature, I employed at first two tubes in the form of U filled with moistened sponge, which were immersed in a large vessel of water kept at a constant temperature. A thermometer was placed in this water, which was continually agitated. A second very delicate thermometer was cemented into the second tube containing the sponge, at the place where the aspirated gas issued; it indicated the temperature of this gas.

I found in this arrangement great inconvenience, which caused me to abandon it. When the air passes through the apparatus, there is always a perceptible difference between the thermometer placed in the current of the gas and that which is immersed in the water of the vessel, so that it becomes difficult to answer for the temperature of the gas and its state of saturation. In order to obtain constant numbers, it is necessary to draw up the saturated air into a large space where the air is apparently in repose. I have adopted the following arrangement:—A cylindrical tin tube of 25 litres capacity (Plate VIII. fig. 2), closed above, is placed on a large plate filled with water; this cylindrical tube has three tubulatures. In the upper tubulature *e* is placed a very delicate thermometer, the bulb of which occupies nearly the centre of the vessel. In the tubulature *f*, the first tube containing pumice-stone moistened with sulphuric acid is fixed, in such a manner that this tube draws up the air into the middle of the case. Lastly, by means of the third tubulature *g*, the cylinder is placed in communication with a balloon O filled with moistened sponge, which the air is obliged to pass through before reaching the cylinder. In order to be more certain of the state of saturation of the air, a cylinder of wire-work, enveloped internally and externally with a piece of moistened linen dipping into the water which covers the bottom of the plate, is placed inside the tin cylindrical tube. A small aperture *o*, in this case, allows of drawing up the air into the centre of the vessel, near the bulb of the thermometer. This apparatus is placed in a chamber the temperature of which varies little, and the experiment is not begun until some time after the apparatus is arranged. The velocity of the current was purposely varied, in order to ascertain whether this exercised a real influence upon the quantity of humidity found. Two experiments were made at the same temperature; one with a current continued for forty-five minutes; the

second with a current which lasted three hours. The weight of water was found exactly the same in these two experiments.

In ordinary experiments the aspirator was emptied in $1^h\ 15^m$ to $1^h\ 30^m$. Every five minutes the thermometer placed in the case was read off at a distance with a telescope, and the mean of the temperatures noted down during the experiment was adopted as the temperature of the saturated air. These temperatures, moreover, varied very little,—one or two-tenths of a degree at most. When the vessel ceased to run, a few minutes were allowed to elapse for the air of the aspirator to take an equilibrium of pressure with the external air, the stopcock *r* was closed, and at the same instant the thermometer T of the aspirator and the barometer were noted. The two absorbing tubes were then detached and weighed.

In these experiments I employed indifferently two aspirators, which I shall designate 1 and 2. These aspirators were accurately gauged by weighings. The aspirator 1 contained 58699·8 grms. of water at the temperature 18°·93; it would contain 58779 grms. of water with the density which the latter possesses at the temperature of 4°. The aspirator 2 contained 57457·5 grms. of water at the temperature 16°·62; it would contain 57513 grms. of water at 4°.

We shall admit 0·0000366 for the coefficient of the cubic dilatation of the sheet-iron. The volume of the aspirators at the temperature of 0° is therefore—

For 1. . . . . 58738 cubic centimetres.
For 2. . . . . 57480 ... ...

In order to obtain the quantity of water contained in the air saturated at 0°, I employed the following arrangement:—A tin tube (fig. 3) $0^m{\cdot}55$ long and $0^m{\cdot}10$ in diameter, bears in its axis a tube *a b* $0^m{\cdot}02$ in diameter. This tube is open at its two ends; a lateral tubulature *c d* connects the tube *a b* with the external air. The first tube, containing pumice-stone moistened with sulphuric acid, is fitted into this tubulature by means of a cork. The tube *a b* is corked at *a*. The case is filled with pounded ice; the water proceeding from the melting of the ice runs off by the stopcock *r*.

When the aspirator is in action the external air is drawn through the ice, which lowers it to 0°; it penetrates into the tube *a b* by the lower aperture *b*, and thence it passes into the drying tubes by the tubulature *c d*.

Let—

t be the mean temperature of the air during the experiment;

f, the elastic force of the aqueous vapour in a state of saturation corresponding to that temperature;

t', the temperature of the aspirator at the end of the experiment;

f', the elastic force corresponding to the vapour in a state of saturation;

H, the barometric height reduced to 0° at the end of the experiment;

α, the coefficient of dilatation of the air;

k, that of the sheet-iron;

V_0, the volume of the aspirator at 0°.

The volume of the aspirator at the temperature t' will be $V_0(1+kt')$: that is the volume of the air aspirated when it fills the aspirator; but this volume of air is saturated with aqueous vapour; consequently the air alone, only supports a pressure $H-f'$; when this same air is in the cylindrical tube it exerts an elastic force $H-f$. Thus its volume is, in this last instance,—

$$V_0(1+kt')\cdot\frac{H-f'}{H-f}.$$

The temperature of this air is t when it is in the cylindrical tube, t' when it is in the aspirator; consequently its volume, under circumstances identical to those which exist in the cylinder, is—

$$V_0(1+kt')\cdot\frac{H-f'}{H-f}\cdot\frac{1+\alpha t}{1+\alpha t'}.$$

If we designate by ω the weight of the cubic centimetre of air at 0° and under the pressure of $0^{m}\cdot760$, and by δ the density of the aqueous vapour taken in relation to that of the air, supposing that the vapour in a state of saturation in the air follows the same law of dilatation and of pressure as the air, we shall have for the weight of the vapour in this volume of air,—

$$V_0(1+kt')\cdot\frac{H-f'}{H-f}\cdot\frac{1+\alpha t}{1+\alpha t'}\cdot\omega\delta\frac{1}{(1+\alpha t)}\cdot\frac{f}{760}.$$

Equalizing this expression to the weights found by experiment, we obtain a series of equations by which we can determine δ, and we may ascertain for certain whether that value is constant for all the temperatures.

I have preferred calculating by means of this formula the weight of the vapour which must be in the air, supposing

$\delta = 0{\cdot}622$, that is to say, equal to the theoretical density, and comparing this weight with that which was obtained by direct weighing.

The following table contains all the results which have been obtained. The experiments at 0° (from 1 to 9) were made in ice, as has been said at page 621; the experiments from 10 to 16 were made in a cellar, the temperature of which varied very little; all the others were made at the ambient temperature of the air in the different seasons of the year.

	Number of the aspirator.	Barometer at the end of the experiment. H_0.	Final temperature in the aspirator. θ.	Temperature of the saturated space. t.	Weight of the vapour.		Difference.
					Observed. P.	Calculated. P′.	
		mm	°	°	gr.	gr.	gr.
1	2	745·00	6·75	0·00	0·271	0·2737	−0·003
2	2	744·76	7·31	0·00	0·273	0·2730	0·000
3	2	748·80	7·14	0·00	0·269	0·2732	−0·004
4	2	748·76	8·87	0·00	0·268	0·2712	−0·003
5	2	748·77	7·76	0·00	0·273	0·2725	0 000
6	2	740·83	7·97	0·00	0·272	0·2722	0·000
7	2	740·65	8·18	0·00	0·273	0·2720	+0·001
8	2	744·19	7·44	0·00	0·272	0·2729	−0·001
9	2	745·74	7·42	0·00	0·271	0·2729	−0·002
10	1	752·79	15·02	14·81	0·734	0·7437	−0·010
11	1	753·72	14·89	14·67	0·731	0·7377	−0·007
12	1	754·72	14·82	14·65	0·731	0·7367	−0·006
13	1	757·60	14·49	14·38	0·721	0·7248	−0·004
14	1	755·51	14·62	14·54	0·726	0·7319	−0·006
15	1	747·27	14·23	14·10	0·710	0·7123	−0·002
16	1	747·99	14·29	14·29	0·720	0·7212	−0·001
17	1	752·38	6·14	5·85	0·424	0·4236	0·000
18	1	751·94	5·79	6·48	0·439	0·4431	−0·004
19	1	756·19	6·75	6·63	0·441	0·4447	−0·004
20	1	756·75	7·54	7·48	0·464	0·4711	−0·007
21	1	754·75	7·05	7·22	0·459	0·4637	−0·005
22	1	754·51	7·10	7·53	0·472	0·4736	−0·002
23	1	748·08	7·03	6·64	0·441	0·4456	−0·005
24	1	763·06	14·12	13·20	0·666	0·6718	−0·006
25	1	765·76	13·40	12·88	0·653	0·6598	−0·007
26	2	755·36	21·07	19·77	0·965	0·9723	−0·007
27	2	757·91	20·56	19·16	0·930	0·9376	−0·007
28	1	762·02	20·19	18·93	0·941	0·9423	−0 001
29	1	760·69	20·04	18·93	0·943	0·9431	0·000
30	2	759·99	19·89	18·97	0·922	0·9293	−0·007
31	2	758·15	20·37	18·84	0·918	0 9196	−0·002
32	2	758·17	19·91	19·00	0 926	0·9310	−0·005
33	2	751·75	22·89	20·57	1·010	1·0133	−0·003
34	2	753·53	22·30	21·52	1·072	1·0791	−0·007
35	1	753·63	21·91	21·56	1·104	1·1079	−0·004
36	1	760·66	21·43	20·33	1·020	1·0276	−0 008
37	2	760·25	21·31	20·42	1·008	1·0121	−0 004
38	2	756·48	21·35	20·32	0·999	1·0054	−0·006
39	1	756·03	20·76	20·46	1·031	1·0398	−0·009
40	2	761·21	19·80	24·27	1·285	1·2977	−0·012
41	2	761·04	20·01	25·46	1·393	1·3952	−0·002
42	1	764·30	20·71	20·52	1·041	1·0440	−0·003

TABLE continued.

	Number of the aspirator.	Barometer at the end of the experiment. H_0.	Final temperature in the aspirator. θ.	Temperature of the saturated space. t.	Weight of the vapour.		Difference.
					Observed. P.	Calculated. P'.	
		mm	°	°	gr.	gr.	gr.
43	1	764·82	20·85	20·43	1·031	1·0374	−0·006
44	1	764·10	20·83	20·75	1·058	1·0586	−0·001
45	2	757·80	21·60	21·40	1·072	1·0752	−0·003
46	2	756·35	21·57	21·55	1·083	1·0855	−0·002
47	1	752·05	24·80	24·93	1·342	1·3456	−0·004
48	1	752·07	24·50	24·17	1·280	1·2880	−0·008
49	1	752·38	24·18	23·42	1·227	1·2380	−0·011
50	1	752·13	24·10	23·37	1·220	1·2338	−0·013
51	1	758·20	27·27	26·94	1·486	1·4730	+0·013
52	1	758·20	26·89	26·74	1·442	1·4500	−0·008
53	1	761·91	25·63	25·11	1·315	1·3279	−0·013
54	1	761·21	25·91	25·91	1·382	1·3919	−0·010
55	1	750·12	26·74	26·28	1·407	1·4179	−0·011
56	1	749·06	24·61	24·05	1·239	1·2489	−0·010
57	1	749·97	24·99	24·31	1·257	1·2673	−0·010
58	1	750·46	24·84	24·77	1·292	1·3066	−0·014
59	1	753·98	24·14	23·11	1·167	1·1801	−0·013
60	1	753·52	24·19	24·49	1·247	1·2602	−0·013
61	1	752·91	24·61	24·83	1·296	1·3117	−0·015
62	1	753·12	24·46	24·82	1·296	1·3122	−0·016
63	1	755·81	23·23	22·59	1·139	1·1487	−0·011
64	1	755·68	23·50	23·34	1·191	1·2022	−0·011
65	1	755·15	23·72	23·80	1·225	1·2358	−0·011
66	1	757·32	24·16	24·18	1·248	1·2625	−0·014
67	1	757·62	23·86	23·85	1·223	1·2383	−0·015
68	1	761·96	22·65	22·44	1·130	1·1414	−0·011

It will be seen in this table that all the numbers calculated are a little greater than those which have been found by direct experiment, and that by the same fraction of the total weight. This fraction is very small; it amounts to about one-hundredth. We may thence conclude that the densities of aqueous vapour in a state of saturation in the air at low temperatures may be calculated from the law of Mariotte, and that the relation of the weight of a volume of this vapour to that of a similar volume of air taken under the same circumstances of temperature and pressure, is rather weaker than the theoretical density of vapour. It is true that the difference which exists between the calculated weights of the vapour and those found by experiment may be explained in another manner. We may admit that the density of vapour in a state of saturation in the air is the same as that which we have found *in vacuo* =0·622, but that the elastic forces of the vapour which I have taken in my table of the tensions of vapour *in vacuo* are too high by a small quantity; this would agree with what we have found above (page 610) by direct ex-

periment on the elastic forces of aqueous vapour in a state of saturation in the air.

However, it is seen that on taking as basis my table of the elastic forces of aqueous vapour *in vacuo*, and admitting that the density of the vapour is constantly equal to 0·622, that of the air under the same circumstances being 1, the calculated weight of the vapour cannot differ from the real quantity by more than a very small fraction, about one-hundredth.

The experiments which I have described may be considered as confirming in a complete manner the accuracy of my table of the elastic forces of aqueous vapour at low temperatures. It is certain that on calculating these experiments with the old tables adopted by physicists, we obtain very conflicting results. The experiments which I have made on the density of aqueous vapour, and which I have just described, were instituted several years ago, and on seeking to calculate them with the old tables, I found the necessity of making new determinations of the elastic forces of aqueous vapour at low temperatures.

Part II.

Processes employed to determine the fraction of Saturation of the Air.

I shall distinguish four principal methods by means of which this determination may be performed:—

1. The chemical method.
2. The method founded upon the indications of hygrometers formed of organic substances which are lengthened by humidity.
3. The method of the condensing hygrometer.
4. The method of the psychrometer, namely, that which is founded upon the observation of the temperatures indicated simultaneously by two thermometers, one with a dry, the other with a moist bulb.

1. *Chemical Method.*

I have little to say on the chemical method, after the details into which I entered at page 617 and the following, to explain the experiments which I made with a view to determine the weight of the water which the air contains when it is saturated. When this method is employed to determine the quantity of moisture which exists in the air in a given place, it is necessary, by means of a long tube, to seek the air in this place and bring

it by aspiration into the drying tubes. A very delicate thermometer is placed in this same spot, which is observed every five minutes from a distance with a telescope. The variations of temperature are, in general, greater and more rapid than those observed in the experiments made with the cylindrical tube, page 620, and it is often found necessary to increase the velocity of the current of the aspirator.

The chemical method does not give the quantity of humidity which exists in the air at a determinate moment, but the mean quantity which the air contained during the experiment. This method is in other respects perfectly accurate, and it is very useful for studying the course of the other hygrometers. I shall give some examples when treating of the psychrometer. But it is too tedious, and it requires too long a manipulation to be often employed in meteorological observations.

2. *Hygrometers formed of Organic Substances or Absorbing Hygrometers.*

A great number of organic substances are lengthened very perceptibly when the quantity of humidity increases in the air, and become shortened when the moisture diminishes. This property has been taken advantage of to construct instruments which immediately indicate the degree of humidity in the air. For this object the most various substances have been proposed; but these instruments were rather hygroscopes than hygrometers; they were devoid of one essential property, that of being capable of comparison; they were therefore soon abandoned.

The hair hygrometer alone escaped the general neglect, which is owing to the perseverance of its inventor, who made numerous experiments to render this instrument capable of comparison, and to give it a graduation by which the fraction of saturation of the air might be calculated.

Saussure's hygrometer was for many years in great favour, but objections were afterwards made to it. Among these were its extreme fragility, and the disturbances in its graduation occasioned by time. Some pretended even that the hair entirely lost its sensibility in a short time. After the death of Saussure artists soon lost the traditions of that able physicist, and often neglected his most important directions. Nevertheless the hygrometer of Saussure offers, for meteorological observations, such great advantages over the other hygrometric methods, that,

notwithstanding the strong prejudices I had against this instrument, I have not hesitated to make numerous experiments to ascertain how far it would furnish precise indications.

I shall recall in a few words the directions of Saussure for the construction of the hair hygrometer. Fine and soft hairs should be selected, cut from a living and healthy head, and not curled. To divest them of grease, a small parcel of the size of a quill is placed in a small piece of linen, which is sown up, and they are boiled in a long-necked flask with 1 litre of water and 10 grms. of crystallized carbonate of soda. The boiling is continued for thirty minutes; then the bag which contains the hairs is taken out, and they are washed, boiling them twice at intervals, for several minutes, in pure water. The cloth is unstitched, and, after having taken out the hairs, they are shaken in various directions in a large vessel filled with cold water, to complete their washing and to separate them from one another; lastly, they are hung up and left to dry in the air. The hairs well-washed in ley are clean, soft, brilliant, transparent, and separated from one another. The weight which stretches the hair should not exceed 0·2 grm. Saussure observes that a hair which is only weighted with 0·6 grm. proceeds at first very regularly, but that it stretches after some time, and that the instrument becomes irregular.

The length of the hair, in the ordinary portable hygrometers, is 24 centimetres. The diameter of the pulley on which the hair is wound should be about 5 millimetres. The point of extreme humidity is ascertained by placing the instrument under a bell-glass whose sides are moistened. To obtain the extreme point of dryness, Saussure recommends to powder with salt of tartar (bitartrate of potass) a plate of sheet-iron bent into a cylinder and heated red-hot; the plate of sheet-iron is then coated with a layer of carbonate of potass which readily absorbs moisture. This cylinder is placed under a very dry glass bell, and the hygrometer is suspended in the middle. The interval between the point of extreme dryness and that of extreme humidity is divided into 100 degrees.

The present makers follow exactly the directions of Saussure for the dimensions of the various parts of the apparatus; but they weight the hair much more. Thus the weight often amounts to 1·8 grm., which is more than three times the maximum weight indicated by Saussure. This circumstance is very

vexatious, as it certainly tends to increase many of the irregularities which are objected to the hair hygrometer.

I have not found anything essential to change in the construction of Saussure; I only think that it would be better to deprive the hairs of grease by leaving them for twenty-four hours in a tube filled with æther. All the solidity of the hairs is thus preserved, and they acquire nearly the same delicacy as if the grease were removed by the boiling solution of carbonate of soda.

I ascertain the point of dryness by placing the hygrometer upright in a cylindrical vessel, at the bottom of which is a thick layer of concentrated sulphuric acid, and I close hermetically the opening at the top by means of a ground glass plate coated with grease. I have found that the concentrated sulphuric acid more rapidly causes complete drying than quicklime or chloride of calcium, and the needle marks two or three degrees more. In the instruments which I employ, the graduation of the scale is arbitrary, and I convert, by calculation, the observed degrees into hygrometric degrees.

The degrees of the hygrometer do not indicate directly the fractions of saturation. In order to obtain these latter, it is necessary to determine, by direct experiments, the relations which exist between the different degrees of the hygrometer and the fractions of saturation. Saussure had already endeavoured to construct a table of this nature. At a later period, MM. Dulong, Gay-Lussac and Melloni investigated this subject, and have determined the elements of these tables by different processes; but all these tables refer to one particular hygrometer, that which was employed by the experimenter; and it remains a question whether the instruments constructed by the mechanician, often under very different conditions, are comparable with one another, from the fact that their fixed points were determined in identically the same manner. Saussure declared that he never observed greater differences than 3 or 4 degrees between two hygrometers constructed according to his method. Admitting this fact as exact for instruments constructed with the greatest care, and under perfectly identical conditions, like those of Saussure, it will be conceded that there is less certainty with the instruments which are met with in the shops.

The first questions which I put to myself are the following:—

1. Are the hygrometers, which are constructed with the same kind of hair, and which have been divested of grease in the same operation, strictly comparable?

2. Are the hygrometers which are constructed with different hairs, but divested of grease in one and the same operation, comparable?

3. Lastly, are the hygrometers which are constructed with hairs of different kinds, divested of grease by different operations, or by different processes, still comparable?

To solve the first of these questions, I observed, under very varied circumstances, a great number of hair hygrometers, recently constructed, which M. Bunten kindly placed at my disposal for this purpose. All these hygrometers had hairs of the same kind, which had been deprived of grease in the same operation.

A first series of observations was made, in the open air, on three of these hygrometers, and on a fourth very old hygrometer, constructed by Paul of Geneva, and belonging to the Physical Cabinet of the Collège de France. These four instruments were regulated simultaneously in the same vessels for their fixed points.

Table I. contains their simultaneous indications:—

TABLE I.

Hygrometers of Bunten.			Hygrometer of Paul.
1.	2.	3.	
72°·0	71°·4	72°·7	60°·9
71·7	71·0	72·7	60·9
75·9	74·8	75·0	64·4
79·1	78·0	77·6	67·1
80·3	79·5	78·4	71·2
77·0	76·7	75·0	71·8
74·8	75·0	74·2	65·6
71·6	71·9	71·1	62·9
75·7	75·7	74·8	66·1
78·0	78·1	77·0	68·6
81·4	80·9	80·3	72·3
80·6	80·3	78·5	71·6
87·6	87·2	85·0	78·6
88·8	88·8	86·3	79·9
90·0	90·0	87·5	82·5
89·1	89·1	87·5	81·7
90·2	90·0	88·3	83·3
86·4	85·2	86·7	80·7
91·6	91·3	88·9	84·1
88·8	87·9	85·2	81·1

A second series of observations was made on three other hygrometers of M. Bunten and on the same hygrometer of Paul, placing the four hygrometers in a cylindrical glass vessel, closed hermetically, and containing a layer of sulphuric acid more or less diluted. The results contained in Table II. were thus obtained :—

TABLE II.

Hygrometers of Bunten.			Hygrometer of Paul.
4.	5.	6.	
10°2	12°0	11°3	10°4
23·0	23·9	23·6	17·5
35·9	38·1	36·2	27·4
55·6	57·6	55·6	42·6
67·3	69·5	66·8	52·0
75·8	77·6	75·1	60·3
82·4	83·6	81·8	66·9
84·8	86·2	84·1	70·0
92·6	93·8	92·4	81·8
98·4	99·5	98·4	92·6

Lastly, five hygrometers of M. Bunten, differing from the preceding, but constructed with the same kind of hairs, were placed simultaneously in the same glass vessel, into which were successively poured mixtures of sulphuric acid and water in variable proportions. The numbers given in Table III. were obtained.

TABLE III.

Hygrometers of Bunten.				
7.	8.	9.	10.	11.
21°1	19°9	18°7	21°3	20°7
41·1	41·3	39·4	42·2	41·1
58·4	58·3	56·2	59·5	58·6
66·3	67·3	65·1	68·7	67·9
79·3	80 7	78·5	82·2	81·4
89·1	90·9	88·6	91·5	91·1
94·2	95·8	94·2	96·0	95·6

It is seen by these tables that the hygrometers of M. Bunten kept pace in a satisfactory manner in all the observations; the greatest difference in fact amounts to only 3°. It will be also observed, that when one of the hygrometers indicates a higher degree than another, a difference in the same direction is maintained in all the other observations.

I conclude from this, *that hygrometers constructed with hairs*

of the same kind, divested of grease in the same operation, do not exactly keep pace, but that nevertheless they do not differ so much in most of the observations as to be regarded as not comparable.

But if we compare in Tables I. and II. the numbers indicated by the hygrometer of Paul with those of Bunten, we find such great differences that it is impossible to regard these instruments as comparable, even in observations in which we should be content with general approximations.

It will be objected that the hygrometer of Paul was very old, and consequently that the hair was altered. It is impossible for me to decide whether this hygrometer presented, when it was first constructed, a course identical with that observed at present; but I can state that this instrument is as delicate and as regular in its indications as any of the hygrometers of modern construction which I have had occasion to examine.

At any rate, this observation alone proves that *hygrometers, constructed with hairs of different nature and prepared in different manners, may present very great differences in their indications, even when their fixed points agree.*

This inequality in their range depends probably in great part on the manner in which the hair is prepared,—perhaps also on the length of time it has been used in the apparatus. I have ascertained, in fact, that hairs of very different natures, but prepared in the same operation, do not present any great irregularities in their range.

Five kinds of hairs, as different as possible in their colour and degree of fineness, were freed from grease in the same operation, following exactly the directions of Saussure. They were mounted on similar frames, and their fixed points were simultaneously determined in the same vessel. Afterwards these instruments were placed in a vessel containing successively more or less concentrated solutions of sulphuric acid.

Hygrometers of Bunten.				
12.	13.	14.	15.	16.
19°·6	23°·4	24°·4	21°·9	21°·5
51·3	54·6	55·0	54·2	53·3
63·4	67·3	67·0	68·3	67·6
77·8	80·6	80·4	80·7	80·3

The hygrometers 13 and 14 kept pace perfectly; the hygro-

meters 15 and 16 exhibited the same coincidence with one another; the hygrometer No. 12 constantly indicated lower numbers. The greatest differences between the indications of these five hygrometers amounted to 5°.

These observations show that it is impossible to calculate a single table which applies exactly to all hygrometers, and it is desirable that observers should have at their disposal a simple process which permits them to construct the table of their hygrometer themselves, and by which they may verify the graduations of their instrument as often as they desire. The process which I shall describe appears to me to satisfy these conditions perfectly.

I prepared mixtures of sulphuric acid and water in definite proportions, so as to produce the following hydrates:—

$SO^3 + 2H^2O$, $SO^3 + 3H^2O$, $SO^3 + 4H^2O$,
$SO^3 + 5H^2O$, $SO^3 + 6H^2O$, $SO^3 + 8H^2O$,
$SO^3 + 10H^2O$, $SO^3 + 12H^2O$, $SO^3 + 18H^2O$.

These mixtures were verified by a strict chemical analysis, and their composition was rectified whenever analysis showed that it differed perceptibly from the composition desired. I determined with the greatest care the elastic forces of the aqueous vapour given by these solutions for temperatures comprised between 0° and 50° C., employing the process described at page 569 (memoir on the tensions of aqueous vapour). I constructed graphically the curves given by these experiments, and by means of three equidistant determinations I ascertained the three constants which enter into the formula $f = a_1 + a_2 \beta^t$.

I obtained in this manner a formula of interpolation for each solution of sulphuric acid.

I constructed by means of these formulæ a general Table, which contains the tensions of aqueous vapour given by these different mixtures of sulphuric acid and water for each degree of the centigrade thermometer, from +5° up to +35°. By the side of the tensions of each solution I have placed, in a contiguous column, the relations of these tensions to those given by pure water at the same temperature; in other words, the fractions of saturation produced by these solutions.

Comparative Table of the Tensions of Aqueous Vapour given by Pure Water and Mixtures of Sulphuric Acid and Water.

Temperatures.	Pure water.	$SO^3 + 2H^2O$.		$SO^3 + 3H^2O$.		$SO^3 + 4H^2O$.	
	Tensions.	Tensions.	Relations.	Tensions.	Relations.	Tensions.	Relations.
°	mm	mm		mm		mm	
5	6·534	0·105	0·0161	0·388	0·0594	0·861	0·1318
6	6·998	0·106	0·0154	0·409	0·0584	0·922	0·1317
7	7·492	0·108	0·0147	0·430	0·0573	0·985	0·1315
8	8·017	0·110	0·0140	0·452	0·0564	1·053	0·1313
9	8·574	0·112	0·0133	0·476	0·0555	1·125	0·1312
10	9·165	0·115	0·0126	0·501	0·0546	1·200	0·1309
11	9·792	0·118	0·0121	0·527	0·0538	1·280	0·1307
12	10·457	0·121	0·0116	0·556	0·0531	1·364	0·1304
13	11·162	0·124	0·0112	0·586	0·0525	1·454	0·1303
14	11·908	0·127	0·0107	0·617	0·0518	1·548	0·1300
15	12·699	0·131	0·0103	0·651	0·0513	1·648	0·1298
16	13·536	0·135	0·0100	0·687	0·0507	1·753	0·1295
17	14·421	0·139	0·0097	0·725	0·0503	1·865	0·1293
18	15·357	0·144	0·0094	0·765	0·0498	1·983	0·1291
19	16·346	0·149	0·0091	0·808	0·0494	2·108	0·1289
20	17·391	0·154	0·0088	0·853	0·0491	2·241	0·1288
21	18·495	0·159	0·0086	0·901	0·0487	2·380	0·1287
22	19·659	0·165	0·0084	0·952	0·0484	2·528	0·1286
23	20·888	0·171	0·0082	1·006	0·0482	2·684	0·1285
24	22·184	0·177	0·0080	1·064	0·0479	2·849	0·1284
25	23·550	0·184	0·0078	1·125	0·0478	3·024	0·1284
26	24·988	0·191	0·0076	1·190	0·0476	3·209	0·1284
27	26·505	0·199	0·0074	1·258	0·0475	3·405	0·1284
28	28·101	0·207	0·0073	1·331	0·0474	3·611	0·1285
29	29·782	0·216	0·0072	1·408	0·0473	3·830	0·1286
30	31·548	0·225	0·0071	1·490	0·0472	4·061	0·1287
31	33·406	0·235	0·0070	1·577	0·0472	4·305	0·1289
32	35·359	0·245	0·0069	1·670	0·0472	4·564	0·1291
33	37·411	0·256	0·0068	1·767	0·0472	4·838	0·1293
34	39·565	0·268	0·0067	1·871	0·0473	5·127	0·1297
35	41·827	0·280	0·0067	1·981	0·0474	5·432	0·1299

Temperatures.	Pure water.	$SO^3 + 5H^2O$.		$SO^3 + 6H^2O$.		$SO^3 + 8H^2O$.	
	Tensions.	Tensions.	Relations.	Tensions.	Relations.	Tensions.	Relations.
°	mm	mm		mm		mm	
5	6·534	1·294	0·1980	2·137	0·3271	3·168	0·4848
6	6·998	1·399	0·1999	2·296	0·3281	3·398	0·4856
7	7·492	1·510	0·2015	2·464	0·3289	3·643	0·4862
8	8·017	1·628	0·2031	2·641	0·3294	3·902	0·4867
9	8·574	1·753	0·2045	2·829	0·3299	4·176	0·4870
10	9·165	1·885	0·2057	3·029	0·3305	4·466	0·4873
11	9·792	2·025	0·2068	3·240	0·3309	4·773	0·4874
12	10·457	2·173	0·2078	3·463	0·3312	5·098	0·4875
13	11·162	2·331	0·2088	3·699	0·3314	5·443	0·4876
14	11·908	2·498	0·2098	3·950	0·3317	5·808	0·4877
15	12·699	2·674	0·2106	4·215	0·3319	6·194	0·4877
16	13·536	2·861	0·2114	4·495	0·3321	6·603	0·4878
17	14·421	3·059	0·2121	4·793	0·3324	7·036	0·4879
18	15·357	3·270	0·2129	5·107	0·3328	7·495	0·4880
19	16·346	3·492	0·2135	5·440	0·3328	7·980	0·4881

TABLE continued.

Temperatures.	Pure water.	$SO^3 + 5H^2O$.		$SO^3 + 6H^2O$.		$SO^3 + 8H^2O$.	
	Tensions.	Tensions.	Relations.	Tensions.	Relations.	Tensions.	Relations.
°	mm	mm		mm		mm	
20	17·391	3·728	0·2145	5·792	0·3329	8·494	0·4882
21	18·495	3·977	0·2152	6·166	0·3331	9·039	0·4882
22	19·659	4·243	0·2157	6·561	0·3337	9·615	0·4888
23	20·888	4·523	0·2164	6·979	0·3342	10·226	0·4894
24	22·184	4·820	0·2173	7·422	0·3345	10·872	0·4900
25	23·550	5·135	0·2180	7·892	0·3351	11·557	0·4904
26	24·988	5·469	0·2189	8·388	0·3357	12·282	0·4915
27	26·505	5·822	0·2196	8·914	0·3363	13·050	0·4924
28	28·101	6·197	0·2205	9·471	0·3370	13·862	0·4933
29	29·782	6·594	0·2214	10·060	0·3378	14·723	0·4944
30	31·548	7·014	0·2223	10·684	0·3387	15·635	0·4956
31	33·406	7·459	0·2232	11·345	0·3396	16·600	0·4969
32	35·359	7·933	0·2243	12·045	0·3406	17·622	0·4984
33	37·411	8·432	0·2254	12·785	0·3417	18·704	0·4999
34	39·565	8·962	0·2265	13·569	0·3429	19·850	0·5017
35	41·827	9·524	0·2277	14·400	0·3443	21·063	0·5036

Temperatures.	Pure water.	$SO^3 + 10H^2O$.		$SO^3 + 12H_2O$.		$SO^3 + 18H^2O$.	
	Tensions.	Tensions.	Relations.	Tensions.	Relations.	Tensions.	Relations.
°	mm	mm		mm		mm	
5	6·534	4·120	0·6305	4·428	0·6777	5·478	0·8384
6	6·998	4·416	0·6310	4·787	0·6841	5·879	0·8401
7	7·492	4·728	0·6311	5·164	0·6892	6·300	0 8409
8	8 017	5·059	0 6309	5·562	0·6935	6·745	0·8413
9	8·574	5·408	0·6307	5·980	0·6974	7·216	0·8416
10	9·165	5·777	0·6303	6·420	0·7005	7·712	0·8414
11	9·792	6·166	0·6297	6·883	0·7029	8·237	0·8412
12	10·457	6·578	0·6290	7·371	0·7049	8·790	0·8406
13	11·162	7·013	0·6283	7·885	0·7064	9·374	0·8398
14	11·908	7·473	0·6276	8·425	0·7075	9·991	0·8390
15	12·699	7·958	0·6268	8·995	0·7083	10·641	0·8379
16	13·536	8·471	0·6257	9·592	0·7086	11·329	0·8370
17	14·421	9·014	0 6248	10·222	0·7088	12·054	0·8359
18	15·357	9·586	0·6238	10·885	0·7088	12·820	0·8348
19	16·346	10·191	0·6234	11·583	0·7086	13·628	0·8337
20	17·391	10·831	0·6227	12·317	0·7082	14·482	0·8327
21	18·495	11·506	0·6223	13·090	0·7078	15·383	0·8317
22	19·359	12·220	0·6216	13·904	0·7073	16·334	0·8309
23	20·888	12·974	0·6209	14·760	0·7066	17·338	0·8300
24	22·184	13·771	0·6207	15·661	0·7059	18·397	0·8293
25	23·550	14·613	0·6204	16·610	0·7053	19·516	0·8287
26	24·988	15·503	0·6204	17·608	0·7047	20·697	0·8283
27	26·505	16·443	0·6203	18 659	0·7040	21·944	0·8279
28	28·101	17·436	0·6205	19·765	0·7034	23·260	0·8277
29	29·782	18·485	0·6208	20·929	0·7027	24·650	0·8277
30	31·548	19·594	0·6211	22·154	0·7022	26·117	0·8278
31	33·406	20·765	0·6216	23·443	0·7018	27·666	0·8282
32	35·359	22·003	0·6223	24·800	0·7014	29·300	0·8286
33	37·411	23·311	0·6231	26·228	0·7011	31·025	0·8293
34	39·565	24·692	0·6241	27·732	0·7009	32·847	0·8302
35	41·827	26·152	0·6252	29·314	0·7008	34·770	0·8313

The following is the use of this table in the graduation of the hair thermometer:—The extreme point of humidity is noted on the hygrometer. With respect to the extreme point of dryness, I considered it perfectly useless to determine it, for there is never occasion to approach it in the observations. Moreover, I regard the point at which the hygrometer stops in air completely dry as not belonging to the hair in its normal state; this point is only attained after many days, a long while after the air has been completely dried. This circumstance sufficiently proves that in completely dry air the hair experiences an abnormal contraction, which perhaps occurs indefinitely; for I have observed in a hygrometer placed in a glass over concentrated sulphuric acid, that the contraction still continued at the end of three months, in a manner very little perceptible, it is true, for it required more than a fortnight for the needle to describe 1°.

I will suppose that the hygrometer is to be employed in a country in which the fraction of saturation of the air never descends lower than $\frac{1}{4}$th; I commence my graduation only from that point. I place the hygrometer in a cylindrical glass vessel, Pl. VIII. fig. 4, the upper aperture of which is perfectly closed with a glass plate. I put some pure water at first at the bottom of this vessel, then successively layers of 2 to 3 centimetres of solutions of sulphuric acid,

$$SO^3 + 18H^2O, \quad SO^3 + 12H^2O, \quad SO^3 + 10H^2O,$$
$$SO^3 + 8H^2O, \quad SO^3 + 6H^2O, \quad SO^3 + 5H^2O;$$

and I note the degrees which the hygrometer indicates in these different cases, as well as the temperature given by the thermometer fixed on the hygrometer at the moment of the observations.

I now take from the table the fractions of saturation which correspond, for each of the solutions, to the observed temperatures. In this manner I obtain the degrees indicated by the hair hygrometer for fractions of saturation exactly determined, and nearly equidistant in the scale. I have consequently all the necessary elements to calculate by interpolation the table of my hygrometer.

The graduation of the hygrometer may be thus made by every observer. The preparation of the normal solutions of sulphuric acid presents no difficulty; the best mode of preparing them consists in taking some concentrated sulphuric acid of commerce

and adding to it a certain quantity of water, so as to bring it to the state of $SO^3 + 4H^2O$; during this operation much heat is disengaged, and there is always water converted into a state of vapour, so that the liquor does not present the exact strength. Its composition is determined with the greatest care by chemical analysis. This liquor, the strength of which is accurately determined, is afterwards employed to form all the other solutions. These liquors may be preserved for a very long time in stoppered bottles, and they may be employed to verify the graduation of the instrument as often as is desired.

The most essential precaution consists in placing the vessel containing the hygrometer in a spot where the temperature alters only very slowly, in order that the liquor may fairly present the temperature indicated by the thermometer. To effect this object, I place the glass in a wooden box having a small lateral door, which is only opened at the moment of the observation.

It is easy to fit to the lid of the glass vessel, fig. 4, a metallic mounting which allows of making a complete vacuum by means of the air-pump. I have thus ascertained that the hygrometer indicates precisely the same degree in the air and *in vacuo*, when it is in presence of the same solution and at the same temperature; but *in vacuo* its course is much more rapid, and a few minutes are sufficient for it to attain its stationary position, even when the fraction of saturation is very small.

I have employed, in forming the table of the hygrometers, another process more complicated in execution, but which allows of obtaining the graduation of the hygrometer in a very short time, and of studying with great precision this graduation at different temperatures.

A glass bell V V′, of about 15 litres in capacity, Pl. VIII. fig. 5, rests upon a cast-iron pedestal. This pedestal has a groove, in which a very fusible cement is poured; the bell is thus closed hermetically from below. This bell carries a mounting A with several tubulatures. Into the central tubulature *o* a very accurate thermometer is fixed; to the second tubulature are soldered a first leaden tube *c d*, which communicates with a barometrical manometer, and a second tube *e f*, which communicates with an air-pump. Lastly, the third tubulature has a stopcock *r*; into this tubulature is cemented a small balloon containing water. The bell is arranged in a large glass vessel full of water. This vessel is itself placed in a cast-iron vessel full of water, which can

be heated by a spirit-lamp, when it is desired to keep the water surrounding the bell at a stationary temperature higher than that of the ambient air.

I placed four hygrometers under the bell; two hygrometers mounted with hairs prepared with the solution of carbonate of soda, one hygrometer with a hair cleansed by æther, and lastly, a fourth hygrometer mounted with a filament of silk. The vacuum is made the first time by leaving the stopcock r open; then the stopcock r is closed, and a vacuum formed several times, by each time letting in dry air very slowly: the bell is thus dried perfectly. Finally, a vacuum is made for the last time as perfect as possible, and the air-pump is detached. The difference in the height of the two columns of the barometric manometer is measured by the cathetometer; the elastic force of the dry air remaining in the apparatus is thus obtained. It is ascertained that the vacuum is maintained in an absolute manner.

In order to introduce a small quantity of moisture into the bell, the stopcock r is opened for a few instants, and then closed again. The tension of the vapour introduced is measured by the increase of the difference of level of the two columns of mercury. The water of the bell is frequently stirred, and kept at a stationary temperature. The hygrometers assume their state of equilibrium very promptly. When it is well-established, their indications and the temperature of the thermometer are noted, and the elastic force of the vapour measured.

To introduce a fresh quantity of vapour, the stopcock r is opened, and is then closed; the same determinations are recommenced, and so on, until the space is brought to a state of saturation. The temperature not having perceptibly changed during the experiments, a table of degrees of the hygrometer is obtained for the different fractions of saturation corresponding to one and the same temperature. It is easy to make a second series of determinations at a higher temperature, drying the bell again, and operating in the manner just described. It may then be ascertained whether the two tables obtained are identical.

When it is only required to make the table of one hygrometer, the bell need not be kept in water, and the experiments may be made at the temperature of the ambient air, provided that this temperature is somewhat high, for at too low temperatures the elastic force of the vapour presents very feeble absolute values, which cannot be measured with sufficient precision.

3. *Condensing Hygrometers.*

Le Roy of Montpellier first proposed, with a view to determine the hygrometric state of the air, to cool slowly some water inclosed in a vessel by successive additions of small quantities of ice until a deposit of dew began to form upon the sides of the vessel. The temperature which the water of the vessel indicates at this moment is that which the air would have completely saturated by the quantity of vapour in it. If t represents the temperature of the ambient air, t' that which is indicated by a thermometer immersed in the water of the vessel, f and f' the elastic forces of the aqueous vapour corresponding to those temperatures, $\frac{f'}{f}$ will be the fraction of saturation of the air.

It is difficult, under most circumstances, to find ice to make this experiment. Some physicists have proposed to lower the temperature of the water in the vessel by dissolving in it certain salts, such as the nitrate of ammonia. But when the air is very dry and its temperature is high, it is often difficult to obtain in this way a sufficiently low temperature to produce the deposit of dew.

The process of Le Roy received its first practical application by the construction of Daniell's condensing hygrometer. It is well known that this instrument, fig. 6, consists of two bulbs A and B united by a large curved tube. The bulb A contains some æther, which rather more than half-fills it; a very delicate thermometer is arranged in the tube, so that its reservoir is in the centre of the bulb A and plunges into the upper strata of the liquid. A vacuum is completely made in this little apparatus before closing it by the lamp. The bulb B is enveloped in a piece of cambric, upon which the observer pours some æther, drop by drop, with a pipette. The evaporation of the æther in the air produces a considerable cooling of the bulb B, which causes the distillation of the æther of the bulb A. The æther cools, and may descend below the temperature at which the air would be saturated by the quantity of vapour existing in it, at the moment. Some dew will therefore be seen to form upon the bulb A. To render the first deposit of dew more apparent, the bulb A is ordinarily constructed with a glass deeply coloured with cobalt, or it is coated with a brilliant gilt ring.

The cooling of the æther in the bulb A principally takes place

at the surface of the liquid where the evaporation occurs, and, as liquids are bad conductors of heat, there is always a marked difference of temperature between the upper layers of the liquid and the lower layers. Thus the deposit of dew always commences on a ring which surrounds the surface of the liquid, and it is not till afterwards that this deposit extends over the whole surface of the bulb. It is necessary therefore to place the reservoir of the thermometer in the upper layer of the liquid, and to make the dimensions of this reservoir very small, in order that the retardation of its temperature over that of the ambient liquid may be as little as possible. But in making this reservoir of very small dimensions the length of the degree of the thermometer is much diminished, and there is more uncertainty in reading off the instrument.

In skilful hands, Mr. Daniell's apparatus may give the temperature of the dew-point approximately, but its absolute exactness cannot be relied on. This apparatus in fact presents several inconveniences, which I will enumerate.

1. The æther presents notable differences of temperature in its different layers; the temperature of the upper layer is lower than that of the inferior layers. Supposing the thermometer to be of extreme delicacy, which is far from being the case, it would still only indicate the mean temperature of the layers in which its reservoir is immersed. Now this mean temperature may differ perceptibly from that on which the first deposit of dew depends. The error which may result from this cause is lessened by determining a very slow evaporation of æther, at the moment when the dew-point is approached; but we cannot hope to make it vanish altogether.

2. The manipulation requires the long-continued presence of the observer near the apparatus: this is very inconvenient, for it necessarily influences the hygrometric state of the air and its temperature, especially if the observer is obliged to approach very near to read off the thermometer and to observe the first deposit of dew.

3. The evaporation of a great quantity of æther takes place on the bulb B, in a space extremely near to that in which the deposit of dew upon the bulb A is determined: it is impossible but that this circumstance, and the lowering of the temperature which it causes in the neighbouring layers of air, must occasion a very sensible change in the hygrometric state of the air.

4. The æther employed is never anhydrous æther. The ordinary æther of commerce contains as much as one-tenth of its weight of water. This water is carried in great part by the vapour of æther into a space very close to that in which the deposit of dew is determined. This circumstance again tends therefore to change the hygrometric state.

5. If the temperature is high and the air very dry, it is impossible to produce the deposit of dew upon the bulb A, even by pouring large quantities of æther upon the bulb B; so that in this case the instrument ceases to act. It is evident, moreover, that the inconveniences which I have noticed in 3 and 4, are considerable in proportion to the quantity of æther evaporated.

A great number of modifications of Daniell's apparatus have been suggested; several experimenters have proposed to observe the deposit of dew upon the bulb of the thermometer itself. They have bent the stem of the thermometer, as shown in fig. 7, and adjusted exactly upon the upper part of the bulb a metallic cup, into which the æther intended to produce the cooling is poured; the deposit of the dew is observed upon the naked part of the bulb. It is evident that this arrangement has no advantage over that of Daniell; the indication of the thermometer corresponds to the mean temperature of the different points of the mercury of the reservoir, and not to that of the portion of its envelope on which the deposit of dew is observed, and every one will see that a very marked difference may exist between these two temperatures, especially during the descending and always very rapid course of the thermometer.

The same objections apply to the constructions proposed by M. Pouillet under the names of *Capsule hygrometer* and *Virole hygrometer**, and to the metallic hygrometer of M. Savary†. All these instruments are very inconvenient in one respect, which it is absolutely necessary to avoid. The surface upon which the deposit of the dew is observed is very near, often even the middle of the space in which the vapour of æther is developed, destined to produce the cooling. In all these instruments the object has been to increase the rapidity of the descending course of the thermometer, whereas it is evidently the contrary problem which must be proposed; this course must be rendered very slow, in order to be sure that only a very small difference exists

* *Elémens de Physique*, 4th edition, vol. ii. p. 635.

† *Annales de Chimie et de Physique*, 3rd Series, vol. ii. p. 531.

between the temperature of the side on which the dew is deposited and that indicated by the thermometer.

I believe all these inconveniences are obviated in the instrument which I propose under the name of a *Condensing hygrometer*, and which I have had occasion to try under every variety of circumstances. This apparatus is composed of a very thin and perfectly polished silver cylinder closed at its lower end, *a b c*, fig. 8. This cylinder is 45 millimetres in height and 20 in diameter; it is ground so as to fit accurately to a glass tube *c d* open at both ends. The tube carries a small lateral tubulature *t*. The upper opening of the tube is closed by a cork, through which the tube of a very delicate thermometer passes, occupying its axis; the cylindrical reservoir of this thermometer is placed in the centre of the silver tube. A thin glass tube *f g*, open at both ends, passes through this cork and descends to the bottom of the silver cylinder. Some æther is poured into the tube as far as *m n*, and the tubulature *t* is made to communicate by means of a leaden tube with an aspirator of the capacity of 3 to 4 litres, filled with water. The aspirator is placed near the observer, whilst the condensing hygrometer is removed as far as is desired.

On allowing the water to run from the aspirator, the air penetrates by the tube *g f*, and traverses the æther in bubbles, which it cools by carrying off the vapour; the refrigeration is rapid in proportion to the escape of the water; the whole mass of æther presents moreover a sensibly uniform temperature, because it is actively agitated by the passage of the bubbles of air. In less than a minute the temperature is lowered sufficiently to determine an abundant deposit of dew. The thermometer is at this moment observed by means of a telescope. I will suppose that this thermometer indicates 12°; it is clear that this temperature is lower than that to which the saturation of the air really corresponds. The stopcock *r* of the aspirator is now closed, the passage of the air stops, the dew disappears after a few instants, and the thermometer rises. I will assume that it marks 13°. This point is higher than the dew-point. I open the stopcock *r* a very little, so as to determine the passage of very few bubbles of air through the æther; if, nevertheless, the thermometer continues to rise, I open the stopcock still more, and I cause the thermometer to descend to 12°·9; by closing the stopcock a little more, it is easy to arrest the descent and

to cause the thermometer to remain stationary at 12°·9 as long as is desired. If no dew is formed, after a few instants it is clear that 12°·9 is higher than the dew-point. I descend now to 12°·8, and keep the thermometer at that point, regulating the escape of the water suitably. I will suppose that the metallic surface tarnishes after a few instants; I conclude that 12°·8 is lower, and that 12°·9 is higher than the temperature to which the saturation corresponds. I can obtain a considerable approximation by seeking whether 12°·85 is above or below this point. For this purpose I turn the stopcock r a very little, so that the thermometer ascends very slowly, notwithstanding the passage of the bubbles through the æther, and I observe whether the dew disappears or whether it remains at 12°·85, at which temperature I keep the thermometer stationary for some instants.

All these operations take longer to describe than to perform; with a little practice, three or four minutes are enough to determine the dew-point to within $\frac{1}{20}$th of a degree.

The aspirator has a much greater capacity than is necessary for a single determination. The one of the capacity I have stated suffices to maintain the condenser for above an hour near the dew-point, so that more than ten consecutive determinations may be made.

I made a great number of determinations by means of this instrument in a large amphitheatre, the temperature and hygrometric state of which changed but very slowly, and I always found perfectly identical results in successive determinations.

When observations are made in the open air, it is seen how much the hygrometric state varies from one minute to another, owing to the incessant changes of temperature. When the thermometer of the stationary condenser is kept near the dew-point, the metal is seen to tarnish or resume its lustre, according as the lightest breath comes from either side. The ordinary hygrometers and the psychrometers are by no means sufficiently delicate to indicate these momentary variations.

It is necessary to ascertain very exactly the temperature of the dry air in the point of space the hygrometric state of which is determined. For this purpose, I place a very delicate thermometer in a second small apparatus similar to the first, at least with the difference only that it contains no liquid. This second apparatus is arranged immediately beside the first; it is

extremely useful to judge, *by contrast*, of the slightest changes which occur in the real apparatus. Thus an observer but little practised might fail to distinguish the first very small deposit of dew, if the condensing hygrometer is single; but he will detect it infallibly, on the contrary, if he has at his side a second apparatus serving for comparison.

Fig. 9 of Plate VIII. represents the apparatus, in the state in which I ordinarily arrange it. *a b* is the acting condenser, the tubulature *t* is cemented into a copper tube *t c d*, to which the leaden tube communicating with the aspirator is attached at *d*. The tubulature *t'* of the second apparatus is stopped with a little mastic. If it is feared that the thermometer T' may not indicate with sufficient rapidity the variations of temperature of the air, it may be suspended in the open air, and the silver cylinder serving for comparison be fixed on the tube *c d*.

It is evident that the apparatus just described obviates all the inconveniences which I have noticed in Daniell's hygrometer. Thus:—

1. The thermometer indicates exactly the same temperature as the æther, and all the layers of this liquid present a uniform temperature, from the continual agitation produced by the passage of the bubbles of air; the metallic side on which the dew is deposited has also the same temperature as the æther, because it is very thin, and is in immediate contact with this liquid.

2. The manipulation does not require the observer to be close by; he may, on the contrary, be at the distance of several yards and observe the instrument with a telescope.

3 and 4. No vapour is formed near the point at which the hygrometric state is determined.

5. Much lower temperatures may be obtained than with Daniell's hygrometer. Thus, during the greatest summer heat, I have lowered the thermometer of the condenser several degrees below zero, and have covered the metallic side with a thick layer of hoar-frost.

Lastly, the cost of æther is much less; I may say indeed that this liquid may be entirely dispensed with, and alcohol used instead. This substitution is very important when experiments are made in hot climates, where the preservation of so volatile a liquid as æther is almost impossible.

I have made several experiments, placing in the condenser

some ordinary alcohol, and I have very easily obtained the deposit of dew. The aspiration of the air must in this case be more rapid than with the æther, and the thermometer sinks more slowly. There is no inconvenience in this, because fewer experiments need be made in order to observe exactly the temperature of the dew-point. The greatest inconvenience in the apparatus is the bulk of the aspirator, and the necessity of filling it with water, which is not always easy on a journey. I will remark first, that the vessel I employ is much too large when a single determination is only required; in this case a vessel capable of holding a quart is sufficient; but I am convinced that, with a little practice, the aspirator may be wholly dispensed with.

I terminate the leaden tube with a small mouthpiece similar to that of an ordinary blowpipe; and before this mouthpiece I place a stopcock; the observer blows at first quickly through the æther, so as to bring the liquid to the dew-point; he then stops, lets the dew disappear, then blows more gently, turning the stopcock as required. It is easy by this means to keep the thermometer of the condenser in an almost stationary condition. A practised observer might even dispense with the regulating stopcock, but the experiment is far more easily made with it.

4. *Of the Psychrometer.*

M. Gay-Lussac was the first to propose to determine the hygrometric state of the air by observing the temperatures indicated by a dry thermometer and by a thermometer whose bulb is kept constantly moist*; but he is of opinion that, in order to deduce from these observations the quantity of moisture existing in the air, it will be necessary to construct tables, the elements of which will require numerous experiments.

Since that period, a German physicist, M. August, has investigated this question, and he has published several interesting memoirs, in which he has sought to establish upon theoretical grounds the formulæ according to which may be calculated the elastic force of aqueous vapour existing in the air, from the temperatures indicated by a dry and a moist bulb thermometer in this air. The apparatus, composed of these two thermometers, has been named the *Psychrometer*.

The following are the grounds on which M. August esta-

* *Annales de Chimie et de Physique*, vol. xxi. p. 91.

blished his formulæ*; I give them here somewhat in detail, because the researches of M. August have not been hitherto published in any French work.

M. August admits that the moist bulb of the psychrometer is always surrounded with a stratum of air, which moreover may be of any conceivable thickness, having the same temperature as this bulb, and saturated with moisture. This temperature is lower than that of the external air; M. August supposes that the strata of air which come thus successively in contact with the moist bulb take the temperature of this bulb and are saturated with moisture. These strata, arriving with a temperature higher than that of the bulb, impart to it a certain quantity of heat; but, on the other hand, they evaporate some water on its surface, and consequently take away from the bulb another quantity of heat. The stationary temperature of the moist bulb is established by the equality between these two quantities of heat. According to this, let

ω be the weight of the small layer of air supposed dry at 0° and under a pressure of $0^{m}{\cdot}760$;

h, the height of the barometer;

t, the temperature of the ambient air indicated by the dry thermometer;

t', the temperature indicated by the moist thermometer;

f and f', the elastic forces of the aqueous vapour in a state of saturation for the temperatures t and t';

x, the elastic force of the aqueous vapour actually existing in the air.

In the stratum of air which surrounds the moist bulb, the aqueous vapour exerts an elastic force f', and the air an elastic force $h - f'$. The weight of this dry air is

$$\omega \frac{1}{1 + \alpha t'} \cdot \frac{h - f'}{760}.$$

The aqueous vapour existing in this air is composed of the quantity found in it before the contact of the bulb, and which has x for its elastic force, and of the quantity formed by evaporation.

The first quantity is represented by

$$\omega \delta \frac{1}{1 + \alpha t'} \cdot \frac{x}{760};$$

* Poggendorff's *Annalen*, 2nd series, vol. v. p. 69.

the second by

$$\omega\,\delta\,\frac{1}{1+\alpha t'}\cdot\frac{f'-x}{760},$$

δ representing the density of the aqueous vapour in relation to the air.

If γ represents the calorific capacity of the air, the quantity of heat given out by the dry air of the stratum, in falling from the temperature t to the temperature t', is

$$\omega\,\gamma\,\frac{1}{1+\alpha t'}\cdot\frac{h-f'}{760}\,(t-t').$$

The aqueous vapour which existed in this air parts with a quantity of heat which, designating by k the calorific capacity of the aqueous vapour, is

$$\omega\,\delta\,k\,\frac{1}{1+\alpha t'}\cdot\frac{x}{760}\,(t-t').$$

Lastly, let λ be the latent heat of the aqueous vapour between the temperatures t and t'; we shall have for the heat absorbed by the vapour which forms,

$$\omega\,\delta\,\lambda\,\frac{1}{1+\alpha t'}\cdot\frac{f'-x}{760}.$$

Equating this last quantity of heat to the sum of the two first, we obtain

$$\omega\delta\lambda\,\frac{1}{1+\alpha t'}\cdot\frac{f'-x}{760}=\omega\gamma\,\frac{1}{1+\alpha t'}\cdot\frac{h-f'}{760}(t-t')+\omega\delta k\,\frac{1}{1+\alpha t'}\cdot\frac{x}{760}\cdot(t-t'),$$

or simply,

$$\gamma\,(h-f')\,(t-t')+\delta\,k\,x\,(t-t')=\delta\lambda\,(f'-x);\quad .\quad (1.)$$

whence

$$x=\frac{1+\frac{\gamma}{\delta\lambda}(t-t')}{1+\frac{k}{\lambda}(t-t')}f'-\frac{\frac{\gamma}{\delta\lambda}(t-t')}{1+\frac{k}{\lambda}(t-t')}\cdot h.\quad .\quad .\quad (2.)$$

In this formula it is necessary to know, besides the data themselves of the observation,—

1. The specific heat γ of the dry air: M. August admits it to be equal to 0·2669, according to the experiments of Laroche and Bérard;

2. The specific heat k of the aqueous vapour: M. August supposes it equal to that of the air, for want of a better datum;

3. The density δ of the aqueous vapour: M. August admits

it to be equal to 0·6235, according to the experiments of M. Gay-Lussac;

4. The latent heat λ of the aqueous vapour between the temperatures t and t'. M. August at first admitted Southern's law for this datum, and he supposed $\lambda = 550$; subsequently he adopted Watt's law, that is to say, he supposed that this quantity is represented by $640 - t'$.

Substituting these numbers and neglecting some very small quantities, M. August obtains the numerical formula*

$$x = f' - \frac{0{\cdot}558\,(t-t')}{640-t'}\,.\,h. \quad . \quad . \quad . \quad . \quad (A.)$$

We shall modify some of the preceding numerical data. Let us suppose the density δ of the aqueous vapour equal to 0·622, that is to say, equal to the theoretical density, and the latent heat of the steam represented by $610 - t'$, on substituting these numbers in the formula (2.), and supposing $\frac{\delta}{\lambda} = k = 0{\cdot}2669$, we shall have

$$x = \frac{1 + \frac{0{\cdot}2669}{0{\cdot}622\,.\,\lambda}\,(t-t')}{1 + \frac{0{\cdot}2669}{\lambda}\,(t-t')}\,f' - \frac{\frac{0{\cdot}2669}{0{\cdot}622\,.\,\lambda}\,(t-t')}{1 + \frac{0{\cdot}2669}{\lambda}\,(t-t')}\,.\,h,$$

or, neglecting the minute quantities,

$$x = f' - \frac{0{\cdot}429\,(t-t')}{610-t'}\,.\,h. \quad . \quad . \quad . \quad . \quad (B.)$$

M. August has sought to verify the accuracy of his formula by comparative experiments which he has made with the psychrometer and Daniell's hygrometer. He cites similar experiments made by other persons, and he finds in all the cases a sufficient agreement between the elastic force of the vapour deducted from the observation of the temperature of the dew-point and that which he determines by means of the formula (A.) from observation of the psychrometer.

M. August finds also a complete verification of his formula in the experiments formerly made by M. Gay-Lussac on the cold produced by the evaporation of water on the surface of the bulb of a thermometer placed in a current of dry air†.

To obtain the formula which applies to this last case, we must suppose $x = 0$ in the equation (1.); the latter then becomes

$$\gamma\,(h-f')\,(t-t') = f'\,\lambda\,\delta. \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

* *Ueber die Fortschritte der Hygrometrie*; August, p. 30.

† *Ann. de Chimie et de Phys.* 2nd series, vol. xxi. p. 82.

If we substitute in the place of f' the function $\varphi(t')$, which expresses the elastic force of the aqueous vapour in the state of saturation relatively to the temperature, we shall have an equation in t' which, resolved by relation to that quantity, will give the temperature to which a thermometer will fall whose bulb is constantly moistened, when this thermometer is placed in a current of dry air of a temperature t. But the function $\varphi(t')$ is too complicated for us to be able to resolve the equation in t'; we must reverse it, suppose successively

$$t' = 0 = 1 = 2 \ldots,$$

and resolve the equation by relation to t. We thus obtain the temperatures t and t' of two thermometers, the first dry, the second moist, placed in the same current of dry air. The intermediate numbers may be calculated by a simple proportional interpolation. The equation (3), resolved by relation to t, gives

$$t = t' + \frac{f' \lambda \delta}{\gamma (h - f')} = t' + \frac{\lambda}{0{\cdot}429} \cdot \frac{f'}{h - f'},$$

or

$$t = t' + \frac{(610 - t')\, f'}{0{\cdot}429\,(h - f')}.$$

The following table contains some values of t calculated in this manner, supposing $h = 760$ millimetres:

t'.	t.	$t - t'$.	t'.	t.	$t - t'$.
− 5°	0°68	5°68	+ 4°	15°42	11°42
− 4	2·18	6·18	5	17·22	12·22
− 3	3·70	6·70	6	19·08	13·08
− 2	5·35	7·35	7	20·99	13·99
− 1	6·95	7·95	8	22·96	14·96
0	8·65	8·65	9	24·97	15·97
+ 1	10·28	9·28	10	27·05	17·05
2	11·95	9·95	11	29·21	18·21
3	13·67	10·67			

The numbers in this table do not differ much from the results observed by M. Gay-Lussac in direct experiments.

The formula (3.) takes no account of the velocity of the current of air; according to that formula the difference of temperature should be the same whatever be that velocity. This result appears *à priori* impossible. I have sought to determine, by direct experiments, the influence of this velocity, and to ascertain whether, starting from a certain value of the velocity, the differences of temperature of the dry and moist thermometers

would become independent of the absolute velocity of the current of air,—a consequence to which we are naturally led by the reasoning applied by M. August to the calculation of the formula of the psychrometer.

With this view I arranged the apparatus as follows :—

A dry thermometer *a* and a thermometer with a moist bulb *b*, fig. 10, are placed in two cylindrical very thin brass boxes A and B. The bulb of the thermometer *b* is covered with a piece of cambric, which is continually kept moist by a cotton wick which is immersed in a small vessel *c*, containing water, and whose neck is hermetically cemented into the lower tubulature of the box B.

A brass tube bent several times E F G, is put in communication with a large tube full of pumice-stone moistened with sulphuric acid to dry the air perfectly, and the tube D communicates with an aspirator of considerable capacity. The experiments were made in the laboratory of M. Reiset, with two aspirators, each of 600 litres in capacity, and which were so arranged that they could aspirate separately, or both at the same time in the same space. The apparatus was placed in a large glass bell filled with water at the ambient temperature, and which was continually agitated. The dry air, before reaching the thermometer *a*, had traversed a very long metallic tube G F E plunged into the water of the vessel, and had acquired the temperature of that water; the latter was moreover very near to the ambient temperature. The stopcock of one of the aspirators was opened partially, the moist thermometer fell immediately; at the end of some time it became stationary: the temperatures indicated by the two thermometers were then noted. To obtain the velocity of the current of air, the water which flowed from the aspirator was received into a glass balloon, having a mark on the neck, and which indicated 5 litres. The number of seconds which the vessel took to fill was counted by a watch marking seconds; it was easy to deduct from this observation the number of cubic centimeters run off in a minute.

A new determination was made exactly in the same manner, opening the stopcock more, and so on. To obtain a very rapid flow, the two aspirators were made to run at once.

The following are the results which were obtained :—

t.	t'.	$t-t'$.	Liquid run off in 1′.	t.	t'.	$t-t'$.	Liquid run off in 1′.
14°·66	7°·28	7°·38	797	21°·48	10°·78	10°·70	815
14·73	6·64	8·09	1096	21·50	10·05	11·45	1117
14·93	5·39	9·54	1466	21·63	9·49	12·14	1523
14·96	5·16	9·80	1845	21·70	9·18	12·52	1947
14·96	4·67	10·29	3045	21·70	8·67	13·03	3019
14·96	4·33	10·63	5067	21·70	8·56	13·14	3330

To compare these numbers more easily, we will refer them to the same temperature t in each of the two series. This temperature will be 14°·96 for the first series, and 21°·70 for the second. For this purpose we shall add to the values of t' quantities equal to those which we should have had to add to the values of t to establish equality. As the quantities to be added are very small, this correction cannot occasion any sensible errors. We shall thus obtain:—

t.	t'.	$t-t'$.	Liquid in 1′.	t.	t'.	$t-t'$.	Liquid in 1′.
14°·96	7°·58	7°·38	797	21°·70	11°·00	10°·70	815
14·96	6·87	8·09	1096	21·70	10·25	11·45	1117
14·96	5·42	9·54	1466	21·70	9·56	12·14	1523
14·96	5·16	9·80	1845	21·70	9·18	12·52	1947
14·96	4·67	10·29	3045	21·70	8·67	13·03	3019
14·96	4·33	10·63	5067	21·70	8·56	13·14	3330

It is seen that, for the same temperature t, the temperatures t' depend much on the velocity of the current of air. If we calculate with the formula (3.) the temperatures t' which correspond to the temperatures t, we find,—

for $t = 14°·96$ $\quad t' = 3°·73$ $\quad t - t' = 11°·23$

$t = 21°·70$ $\quad t' = 7°·36$ $\quad t - t' = 14°·34$

The values of t' which we thus find are still less than those which we have found in our experiments with the more rapid escape of water.

A pretty exact idea may be formed of the course of these experiments by representing them by a graphic curve. We take, on the line of the *abscissæ*, lengths proportional to the velocities of flowing, and on the corresponding ordinates, lengths proportional to the temperatures t' of the moist thermometer. For $v = 0$ we shall evidently have $t' = t$; this is the point at which the curve bisects the axes of the t. If we draw a parallel to the axis of the v, at a distance equal to the value of t', deduced from our formula, we should have an asymptote to the curve, if this

value of t' corresponds to an infinite velocity of the current of air; but I am convinced, that by establishing through the apparatus a current of dry air more rapid than that which we have obtained in the preceding experiments (which is easily done by working A an air-pump), we see the temperature t' of the moist thermometer fall very perceptibly below that which is deduced from the formula. I have in fact obtained in two experiments—

t.	t'.	$t-t'$.	t' calculated by the formula.
18°·91	5°·39	13°·52	5°·91
22°·95	7°·35	15°·60	8°·00

The preceding experiments demonstrate that it is by a fortuitous circumstance that the experiments of M. Gay-Lussac gave numbers differing little from those deduced from the formula; for very different numbers would have been obtained if another velocity of the current of air had been employed. The experiments of M. Gay-Lussac cannot consequently be cited as confirming the accuracy of the formula of M. August.

If the velocity of the current exercises a great influence on the lowering of the temperature of the moist thermometer when the air is completely dry, it is evident that this influence must also be very sensible when the air contains a certain quantity of humidity. To convince myself of this, I made the following experiment:—The apparatus described above was put in communication by its tube E with an aspirator: to the extremity G a long glass tube was fitted, which drew the air from an outer court-yard, immediately by the side of a psychrometer. The aspirator was made to run, and when the moist thermometer had reached its stationary state, the two thermometers a and b of the apparatus, and the two thermometers of the external psychrometer were noted simultaneously. As the same air acts upon the two psychrometric apparatus, it is clear that the formula applied to their simultaneous indications should lead to the same quantity of humidity.

In a second experiment, to obtain a more rapid current of air, two aspirators were employed to aspirate at once; lastly, in a third experiment, a very rapid current was obtained by aspirating the air with an air-pump. The following are the results obtained in this manner:—

Aspiration with	External Psychrometer.				Psychrometer in the apparatus.			
	t.	t'.	$t-t'$.	f.	t.	t'.	$t-t'$.	f.
1843. June 11.	°	°	°	mm	°	°	°	mm
1 Aspirator ...	16·40	12·27	4·13	8·40	14·69	11·17	3·52	7·98
2	16·79	12·39	4·40	8·33	14·77	10·74	4·03	7·44
1	18·15	13·34	4·81	8·69	14·80	11·17	3·63	7·92
June 12.								
Air-pump.....	13·15	10·82	2·33	8·41	14·58	10·52	4·06	7·29
June 13.								
2 Aspirators...	16·10	13·48	2·62	10·09	14·85	12·57	2·28	9·62

In this table it is seen that, when the current of air has been determined by the flowing of the aspirators, or by the air-pump, the elastic force of the vapour calculated with the formula, according to the observations made on the thermometers placed in the apparatus, was always less than that deduced from the observation of the psychrometer placed out of doors: the contrary would certainly have taken place if the current of air had been slow.

From all that has been said it results, that the agitation of the air must exert a very sensible influence on the indications of the psychrometer: it is easy to be convinced of this by a direct experiment. Let a psychrometer be fixed on the circumference of a horizontal wheel to which a very rapid motion is given. It is seen that, during the motion, the dry thermometer rises a small fraction of a degree, but the moist thermometer falls continually several tenths of a degree.

I do not think that the fundamental hypothesis adopted by M. August can be admitted as basis of the calculation of the psychrometer; namely, that all the air which supplies heat to the moist thermometer falls to the temperature t' indicated by the latter, and is completely saturated with humidity. It seems to me probable that the portion of the air which cools does not fall to t', and that it is not saturated with humidity. The relation of the quantity of heat which the air takes from the bulb by evaporation of the water, to the quantity of heat which it loses in cooling, is probably greater in proportion as that air is more dry, because, in this state, it is much more susceptible of humidity than when it approaches its state of saturation.

Lastly, the temperature of the moist bulb is again otherwise influenced than by the immediately ambient air; it is subjected to the radiation of the chamber, the influence of which will be variable according to the state of agitation of the air.

It seems to me impossible to bring all these circumstances into the theoretical calculation of the instrument, and I think it more prudent to employ theoretical considerations only in the investigation of the form of the function, and to determine afterwards the constants by experiments made in fixed conditions. This mode of operation appears to me the more necessary, as there is much uncertainty as to several of the numerical elements which enter into the calculation, especially as to the specific heat of the air, that of the vapour, and the heat absorbed by the water when it is evaporated in the air. I shall indicate, at the conclusion of this memoir, processes which will admit, I think, of determining these elements with precision by direct experiments.

Thus, let us take

$$x = \mathrm{A}f' - \frac{\mathrm{B}\,(t-t')}{\lambda}.h, \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

and let us seek whether this formula, applied to the calculation of the indications of a psychrometer placed in very various circumstances, can give in all cases the real quantity of humidity, by determining agreeably the constants A and B. If the formula thus determined cannot represent the quantity of humidity which exists in all cases, we may suppose A and B functions of t, or of t', or of $(t - t')$ that, for more simplicity, we shall take from the form $a + b\,t$ or $\frac{1}{a + b\,t'}$, &c.

I began by seeking whether the temperature of the moist thermometer did not depend on the form or size of its bulb and the manner in which it is moistened. I ascertained that in air little agitated, in the class room of physics of the Collège de France, which has a total capacity of about 600 cubic metres, a thermometer with a spherical bulb of sufficient size, 17 millimetres in diameter, exhibited constantly a temperature of $0^{\circ}{\cdot}10$ to $0^{\circ}{\cdot}20$ higher than that indicated by two thermometers with very long cylindrical bulbs, placed immediately by the side. In the open air, the difference was maintained in the same direction, but it became weaker. The spherical bulb of the thermometer which I employed in this experiment is much larger than the bulbs commonly are of the thermometers which are employed in the psychrometer; but I have chosen it so purposely, in order to increase the difference, if any existed. I think it may be thence concluded that the form of the bulb exercises only a very feeble influence on the stationary tempera-

ture at which the moist thermometer arrives. I nevertheless prefer thermometers with cylindrical bulbs, because they are much more susceptible of the variations of temperature which occur in the air, and because, for the same mass of mercury, they present a much greater surface to the air.

I have ascertained that the manner of moistening the thermometer also did not exercise any perceptible influence, provided that the quantity of water which reaches the cambric surrounding the bulb is sufficient. When this quantity is greater than that which is evaporated, and consequently a drop of water falls from time to time at the extremity of the bulb, I have still observed no sensible difference. It is evident, moreover, that the quantity of water which arrives in excess must always be very small, otherwise it would not have time to cool by evaporation. The longer or shorter course which this water runs on the cotton wick from the reservoir to the bulb of the thermometer did not seem to me to exercise any perceptible influence, at least within the limits which are not exceeded in the ordinary construction of the psychrometer.

First Series of Experiments.

The thermometrical apparatus employed were a thermometer A with a dry bulb, the reservoir of which was 8 millimetres in diameter and 30 millimetres in length.

A wet thermometer B, whose bulb was 5 millimetres in diameter and 60 millimetres in length;

A wet thermometer C; diameter of the bulb, 7 millimetres; length, 45 millimetres.

These thermometers are fixed at the extremity of a board 2 metres long, the bulbs are 4 decimetres above the board; the other extremity of the board is fixed to the balcony of a window exposed to the north and situated on the first story. These thermometers are in the open air in a large court (large quadrangle of the Collège de France), at a distance of 7 metres above the ground; they are observed with a telescope. By means of an aspirator and a long glass tube the air is drawn out at a short distance from the thermometers, and this air is made to pass through weighed drying tubes. During the flowing of the aspirator the indications of the thermometers are regularly inscribed every five minutes. The means are taken which enter into the formula of the psychrometer, to calculate the quantities

of humidity, and to compare them with those which have been obtained by direct weighing.

To judge more easily of the course of the experiments I have adopted the formula

$$x = f' - \frac{0{\cdot}429\,(t - t')}{610 - t'} \cdot h.$$

The values $\frac{x}{f}$ of the fraction of saturation inscribed in the table have been calculated with the value of x found by means of this formula.

TABLE I.—*Experiments on the Psychrometer made in the large quadrangle of the Collège de France.*

Dry thermometer A. t.	Moist thermometers. t'.	$t-t'$.	h_0.	Weight of water found. p.	Degrees of saturation. Found. $\frac{p}{P}$.	Calculated. $\frac{x}{f}$.
			SERIES 1.			
°	°	°	mm	grm.		
12·12	7·07	7·10	5·04	764·38	0·270	0·396	0·424
12·54	7·61	7·63	4·92	764·35	0·3035	0·466	0·474
14·07	7·56	7·60	6·49	764·43	0·2595	0·362	0·356
15·24	9·52	9·53	5·72	762·42	0·324	0·420	0·417
16·68	10·06	10·06	6·62	760·42	0·319	0·377	0·396
17·88	8·27	8·30	9·60	754·89	0·1755	0·193	0·197
13·18	8·87	8·97	4·26	756·43	0·340	0·506	0·551
18·08	11·66	11·68	6·41	754·72	0·399	0·438	0·438
18·47	10·60	10·63	7·83	754·36	0·3245	0·344	0·337
18·06	.....	12·51	5·55	751·10	0·436	0·496	0·507
13·12	9·39	9·46	3·69	749·38	0·398	0·597	0·609
9·39	5·62	5·68	3·74	737·09	0·287	0·545	0·554
7·16	5·29	5·31	1·86	748·71	0·332	0·731	0·750
			SERIES II.—Small Psychrometer.			
17·90	11·79	.....	6·11	752·61	0·392	0·439	0·463
17·70	11·71	.....	5·99	752·50	0·405	0·454	0·466
14·51	11·06	.....	3·45	755·57	0·455	0·628	0·646
16·58	12·24	.....	4·34	755·10	0·466	0·563	0·589
16·33	12·34	.....	3·99	754·70	0·485	0·594	0·617
16·05	12·84	.....	3·21	754·65	0·543	0·677	0·685

The fractions of saturation, calculated by means of the formula, agree here in a very satisfactory manner with those which are found by direct weighings. But the agreement was much less perfect in the lower temperatures and in a very humid air, as may be judged by the following Table, which contains experiments made under circumstances quite similar in December 1842. The psychrometer employed in these last experiments

was composed of two thermometers with a spherical bulb of 10 millimetres in diameter. The same apparatus was employed in the second series of the preceding table.

TABLE II.

Thermometer.				Weight of water found.	Degrees of saturation.	
Dry. t.	Moist. t'.	$t-t'$.	h_0.	p.	Found. $\frac{P}{p}$.	Calculated. $\frac{x}{f}$.
°	°	°	mm.	gr.		
7·26	6·51	0·75	772·52	0·391	0·8503	0·896
7·70	6·66	1·04	771·73	0·401	0·8406	0·859
7·10	6·95	0·15	771·87	0·441	0·9626	0·979
8·25	8·10	0·15	768·33	0·4835	0·9783	0·979
9·65	8·89	0·76	766·62	0·473	0·8734	0·904
9·84	8·92	0·92	764·69	0·473	0·8616	0·889
5·64	4·54	1·10	753 50	0·331	0·8035	0·841
6·87	4·67	2·20	753·75	0·278	0·6193	0·694
1·37	1·14	0·23	759·36	0·266	0·9877	0·959
5·65	4·46	1·19	758·67	0·314	0·7576	0·828
0·85	0·29	0·56	755·33	0·2435	0·8183	0·900
7·52	6·22	1·30	748·14	0·361	0·7659	0·826
8·33	6·76	1·57	748·14	0·372	0·7436	0·797
5·80	5·41	0·39	768·22	0·3525	0·8314	0·943
8·56	7·73	0·83	770·13	0·4345	0·8533	0·891

The fractions of saturation calculated are all, with one exception, one-tenth higher than those given by direct experiments, and often in a very marked manner; it is true, that in low temperatures, and for large degrees of humidity, the indications of the psychrometer offer little precision on account of the slight difference of the temperatures indicated by the dry and moist thermometers.

Two other series of experiments were made in enclosed spaces: their object was to demonstrate that the same formula cannot be applied in this case. The first series, Table III., was made in a room 100 cubic metres in size, which the operator, who observed the thermometers from an adjoining room with a telescope, did not enter. The second series, Table IV., was made in the class-room of Anatomy in the Collège de France.

TABLE III.—*Experiments made in an enclosed room in the Collège de France* (*August*, 1843).

t.	t'.	$t-t'$.	h_0.	p.	$\frac{p}{P}$.	$\frac{x}{f}$.
			mm	gr.		
21°·44	17°·44	4°·00	760·13	0·605	0·5649	0·6644
21·65	17·73	3·92	757·03	0·624	0·5743	0·6745
22·06	18·08	3·98	756·75	0·644	0·5775	0·6716
22·47	18·41	4·06	756·27	0·659	0·5769	0·6689
22·39	18·48	3·91	758·50	0·661	0·5816	0·6831
23·52	19·32	4·20	758·49	0·686	0·5652	0·6663
23·38	18·02	5·36	758·61	0·594	0·4930	0·5814
23·73	18·44	5·29	757·40	0·598	0·4889	0·5902
25·75	19·81	5·94	755·33	0·652	0·4731	0·5656
23·44	18·97	4·47	758·28	0·669	0·5530	0·6457

TABLE IV.—*Experiments made in the Class-room of Physics.*

t.	t'.		$t-t'$.	h_0.	p.	$\frac{p}{P}$.	$\frac{x}{f}$.
				mm	gr.		
8°·06	6°·67	6°·69	1°·38	757·39	0·3585	0·7525	0·8187
8·29	6·52	6·55	1·75	762·92	0·344	0·7107	0·7709
9·15	7·23	7·23	1·92	764·98	0·345	0·6738	0·7582
15·71	12·14	12·20	3·54	751·59	0·460	0·597	0·652
16·19	12·49	12·55	3·67	752·35	0·461	0·581	0·645
16·32	12·65	12·71	3·64	751·36	0·463	0·580	0·649
14·78	12·01	11·98	2·78	752·97	0·474	0·653	0·715
15·25	12·34	12·34	2·91	735·43	0·479	0·640	0·706

The fractions of saturation, calculated with the formula, are here much stronger than those deduced from direct weighing of the water contained in the air; in other words, the temperature t', indicated by the moist thermometer, is not lowered enough by the evaporation of the water which occurs at its surface to give in the formula the true elastic force x of the vapour. This circumstance is evidently dependent on the air being much less agitated than the external.

The experiments inserted in Table V., compared with those of Table IV., prove it in a perfectly evident manner. The psychrometer being placed in the class-room of physics, exactly as in the experiments in Table IV., two large windows on the opposite sides were opened. The thermometers, being placed between the two windows, were exposed to a pretty strong current of air. The indications of the apparatus immediately approached those which it would have given in the open air.

TABLE V.—*Experiments in the Class-room of Physics, with the two opposite windows open.*

t.	t'.		$t-t'$.	h_0.	p.	$\frac{p}{P}$.	$\frac{x}{f}$.
°	°	°	°	mm	gr.		
17·49	11·54	11·60	5·92	750·97	0·382	0·444	0·469
17·21	11·50	11·62	5·65	753·06	0·394	0·468	0·486
17·45	11·60	11·71	5·80	752·56	0·389	0·454	0·478
13·01	10·05	10·11	2·93	755·73	0·431	0·665	0·683
14·05	10·72	10·80	3·29	755·68	0·440	0·636	0·658
16·19	11·88	11·95	4·28	755·11	0·450	0·570	0·589
16·20	12·25	12·33	3·91	754·70	0·474	0·598	0·623

These experiments demonstrate in the most evident manner that the same formula is not applicable to these different cases.

I have endeavoured to ascertain whether one and the same formula might be adopted in experiments made *in the open air*, but under very different pressures of the atmosphere. For this it was necessary to perform in very elevated localities the same experiments that I had made at Paris; not having time for these experiments myself, I requested M. Marié, one of my pupils, to perform them.

This young savant made two series of experiments, one at Saint Etienne, in May and June 1843, under a mean barometrical pressure of 705 millimetres; the other, on Mount Pila, under a pressure of 655 millimetres.

The experiments of M. Marié were made by the same methods as my own, but they present much greater irregularities. These experiments were made under unfavourable circumstances; the thermometers often varied several degrees during the same experiment; it then becomes very difficult to value by calculation the mean quantity of moisture, unless the observations of the thermometers are made at very close intervals of time, which unfortunately was not the case in the experiments of M. Marié.

Lastly, M. Izarn has been kind enough to make some experiments in the Pyrenees during the month of July 1844. These last experiments were made by observing, on one hand, the indications of the psychrometer which was employed for the observations in Tables No. I., second series, and No. III., and by determining, on the other hand, the point of saturation of the air by means of my condensing hygrometer.

Psychrometer.			Condenser.	Ho.	Fraction of saturation.	
t.	t'.	$t-t'$.	θ.		Condenser.	Psychrometer.
				mm		
20°12	17°37	2°75	15°39	700	0·7437	0·7632
20·68	16·77	3·91	15·34	...	0·7157	0·6746
20·56	16·91	3·65	14·99	...	0·7047	0·6937
20·92	18·45	2·47	16·62	...	0·7651	0·7903
20·55	18·29	2·26	16·70	...	0·7864	0·8055
20·32	18·22	2·10	16·63	...	0·7942	0·8177
13·50	11·53	1·97	9·22	...	0·7542	0·7937
13·60	11·56	2·04	9·32	...	0·7548	0·7871
13·44	11·51	1·93	9·37	...	0·7652	0·7975
14·13	11·97	2·16	9·43	...	0·7350	0·7786

The experiments of M. Izarn give for $\frac{x}{f}$ rather greater values than those deduced from the observation of the temperature of the dew-point on the condenser. The experiments of M. Marié give, in general, the same result. These determinations show, that by adopting, for the observations made in the open air, the numerical formula

$$x = f' - \frac{0{\cdot}429\,(t - t')}{610 - t'} \cdot h,$$

we obtain elastic forces x a little too high; it would consequently suffice, to approach more to the real values, to replace the coefficient 0·429 by rather a greater coefficient. The coefficient 0·480 gives an almost perfect coincidence between the calculated results and those found by direct observation, in the fractions of saturation which exceed 0·40; but it produces a difference greater than the coefficient 0·429, and in an inverse direction for weaker fractions of saturation. It appears hence to result that the coefficient B of the formula (4) depends on $(t - t')$; this evidently results from the fact that the air carries off proportionally more vapour when it is very dry than when it approaches saturation.

To represent the determinations made in enclosed spaces, like those in Tables III. and IV., it would be necessary to adopt a much higher coefficient.

I shall abstain for the present from establishing a new formula of the psychrometer; I do not consider the elements at my disposal as sufficient; I am engaged on determining by direct experiments the value of λ, that is to say, the latent heat which water absorbs on evaporation in air at a determined tem-

perature t; the value $610 - t$, which I have given above, has been admitted, after numerous experiments which I have made on the latent heat of aqueous vapour under different pressures, and which I shall soon publish. But in these experiments I have never operated under pressures of vapour weaker than $\frac{1}{5}$th of an atmosphere, and these are still much greater than the tensions which we find in atmospheric vapour.

It will be desirable also to make new experiments in very elevated localities, to ascertain whether the second term corrects properly the formula for the variations of h.

The developments which I have just given will suffice to prove that the theory of the psychrometer is not so simple as is generally admitted, and that, to render this instrument really useful for meteorology and physical science, a great number of direct experiments must be instituted, under very various circumstances, to ascertain whether it is *possible* to determine a single formula for the psychrometer, and to obtain the necessary elements to calculate the coefficients.

It is to be wished that scientific men who are interested in the progress of meteorology would engage in these experiments in different climates; and I hope that the discussion in which I have engaged, and the methods which I have put forward in this memoir, may be of some use to them in their researches.

Article XXII.

Opinions relating to the Composition of Organic Substances. By J. Berzelius*.

[From Poggendorff's *Annalen*, vol. lxviii. p. 161.]

No portion of the science of chemistry has given rise to so much difference of opinion as the composition of organic substances. The greater number of those who have occupied themselves with the subject, have often been led by their experiments to quite unexpected modes of combination, have taken up at the moment some peculiar ideas concerning them, and, without noticing the relationship which these may or may not bear to the whole system of the science, have pursued constantly the same course in search of further proof of their own views. In this manner almost innumerable different opinions have been broached. To these I do not intend to add another; but my object in this essay is simply to call attention to the want of unity thus brought into the science, and to the injury which it sustains from these purely fanciful views, to check and restrain the unscrupulous flight of the imagination in theoretical speculations, and to abide steadfastly, whenever it is possible, by that which can in some measure be proved by practical observation. I am prepared in doing this to dispense with the approbation of the many.

Empirical and rational Composition.—The composition of every organic substance can be determined by analysis. The atomic weight of the greater number can also be ascertained with some degree of certainty, by aid of which the number of simple atoms, as likewise the relative number of atoms of each element, can be satisfactorily established. This constitutes the empirical composition of the substance. For instance, the composition of oxamic acid is represented by the empirical formula $C^4H^4N^2O^5$.

Now arises the question, how are these elementary substances coupled together? Can and must this acid be considered as composed on the one hand of 5 atoms of oxygen, and on the other of a compound radical $C^4H^4N^2$? The mode of union of the elements in forming this radical is simple and not improbable; but we know that such is not the composition of the acid, but

* Translated by E. Ronalds, Ph.D.

that it is composed of oxalic acid combined with oxamide as a conjunct. This is its rational composition, and

$$C^2O^3 + NH^2, C^2O^2$$

is its rational formula.

The rational composition of bodies is the highest problem of organic chemistry; but it has only been solved satisfactorily, up to the present time, in the case of a very limited number of organic bodies, notwithstanding it has been the object of all the exertions of those who have occupied themselves with organic chemistry. In endeavouring to ascertain the rational composition of bodies, the greatest caution in drawing conclusions must be combined with the soundest judgement, and it is impossible to make use of too manifold means of proof. Science suffers, and will long suffer, from rational formulæ, which, invented by a lively imagination, have no other proof of their correctness than that they do not actually contradict the result of analysis. For when this latter corresponds to a number of rational formulæ, nothing can be proved from it. What I am about to bring forward in the following pages will clearly show how science is led astray and put into confusion by hasty and unfounded conclusions.

Although the composition of organic bodies, at the first glance, appears to be altogether different from that of the inorganic, yet what we know of the latter is the only unerring guide which we possess to enable us to form an opinion upon the former. In exploring the unknown, our only safe plan is to support ourselves upon the known. This must also be the right way here, and what we already know concerning the laws of combination which regulate inorganic nature, must be taken as a guide in judging the modes of combination in organic nature. Every other mode of procedure allows full scope to fancy, which, varying only with the inventive faculties of the individual, is always ready to build new castles in the air. It is thus that numberless different views are set up, and varied in all kinds of ways, no one following the same rule as the other, they cross and contradict each other in all directions; and this will continue, until we are all agreed by what rule the formation of our judgement should be guided. I therefore repeat, *that the application of that which is already or can hereafter be known concerning the laws of combination amongst elementary bodies in inorganic nature, is the only guide to our researches concerning their mode of combination in organic nature; that by this means alone we can*

hope to arrive at a correct and unanimous opinion concerning the constitution of those bodies which occur in nature or which arise from the action of chemical agents upon them.

These principles, although never positively denied, have also never been generally admitted.

Historical Statement of the Views entertained upon Organic Composition.

The first tolerably satisfactory experiments upon the composition of organic substances were published in 1811 by Thénard and Gay-Lussac. The law of chemical proportions was then only partially developed, and had not attracted the attention of these chemists, who were consequently obliged to determine the relative quantities of the elements in hundredths of the analysed substance. The view to which these experiments led, namely, that those organic substances were neutral, in which, as in starch, sugar, wood, &c., the hydrogen and oxygen were in the same relative proportions as in water, whereas those containing oxygen in excess possessed the properties of acids, and that an excess of hydrogen, classed a substance amongst the resins, oils or spirituous fluids, although in accordance with the results of the analyses, has since been found to be incorrect. Some years afterwards, when I had endeavoured to establish the law of chemical proportions for inorganic substances, I undertook, with a similar object in view, the examination of organic composition. It then appeared that all organic bodies containing oxygen, including those not reckoned amongst the acids, could be made to combine with inorganic oxides in definite and often in multiple proportions, by which means, as in inorganic nature, the atomic weight, and with it a check upon the accuracy of the analytical results, could be obtained. At the same time it was observed that the oxygen of the organic substance was a multiple of the oxygen in the inorganic oxide with which it was combined, and that the amounts of the other constituents corresponded to a certain number of atoms, and could, as in inorganic compounds, be expressed by a formula. This similarity between organic substances containing oxygen and the inorganic oxides, led immediately to the idea that the organic bodies were oxides of compound radicals, whereas the inorganic were oxides of simple elements.

This view I expressed in the second edition of my 'Manual

of Chemistry' (pt. 1. S. 544. Stockholm, 1817), in the following words:—"We find the following to be the difference between organic and inorganic bodies; all oxidized bodies in inorganic nature have a *simple radical*, whereas all organic substances are *oxides of compound radicals*. In vegetable substances these radicals are generally composed of carbon and hydrogen; in animal substances, of carbon, hydrogen and nitrogen. Acids with compound radicals are therefore synonymous with acids of organic origin. In like manner as ammonia is an alkali with a compound radical, *i. e.* of organic origin, being chiefly obtained from the animal kingdom, but nevertheless has the greatest analogy to the alkalies which have a simple radical, and are derived from inorganic nature, so we shall find the same analogy to exist between the acids of organic and those of inorganic origin, and as potash and soda are related to ammonia, so are sulphuric, nitric, and phosphoric acids related to acetic, oxalic and citric acids, &c."

The number of analysed organic substances was confined to those which had been the subject of Thénard and Gay-Lussac's and my own experiments. The view thus put forth was probably considered by the greater number of chemists as premature, for it remained twenty years quite unnoticed.

The notions which in the course of time prevailed were of quite a different nature. Organic bodies were looked upon as binary compounds of elementary substances, or as binary compounds united with an element. Prout endeavoured to show that the greater number of vegetable substances, particularly those used as food by animals, could be considered as combinations of water with carbon in different relative atomic proportions. Thénard and Gay-Lussac had already conceived this idea, although they saw at the same time that it was not tenable. Other chemists began to calculate how organic substances, according to circumstances, might be considered as combinations of two or more binary compounds; carbonic acid, water and carburetted hydrogen, in different proportions. There was no other foundation for these calculations but individual opinion and accordance with the per-centage result of analysis; all the views differed, and now no longer belong to the science, but to its history.

The idea of the union of binary compounds had in the mean time received a strong support from Gay-Lussac's examination

of alcohol and æther; he showed in the year 1816 that these bodies comport themselves in such a manner as to render it probable that 2 volumes of olefiant gas were combined in æther with 1 volume of the vapour of water, and in alcohol with 2. The accordance of this view with the specific gravity of these bodies in the gaseous form, and with the consequent theory of the formation of æther from alcohol by the withdrawal of water, was so complete, that it could scarcely fail to awaken a complete conviction in all such as had not previously formed a decided opinion upon the mode of combination of organic bodies. Further evidence in support of this view was obtained, for instance, by Mitscherlich's examination of hydrated benzoic acid, which he considers a combination of 2 atoms of carbonic acid with 1 atom of a carburetted hydrogen obtained by him from this acid, and which he called Benzine = $2CO^2 + C^{12} H^{12}$.

The discussions upon the composition of the æthers, and more particularly the admirable researches conducted by Dumas himself, or under his guidance, he still retaining the views of Gay-Lussac, afforded me an opportunity, in the annual account of the progress of Chemistry (pp. 189–201) laid before the Royal Academy on the 31st of March 1833, of comparing the two views which were entertained of the composition of organic bodies containing oxygen, namely, that they were oxides of a compound radical or compounds of binary bodies; I there showed that all the combinations of the æthers with acids and salt radicals are equally and perhaps more compatible with the view that æther is the oxide of a compound radical; that this oxide can combine, like an inorganic oxide, with anhydrous acids, both of organic and inorganic origin; that exposed to the action of hydracids its radical is reduced by the hydrogen of the acid, which then, with the separation of water, unites with the salt radical to form a kind of æther, having the same relation to those formed by oxyacids that a halogen salt bears to an oxygen salt. I then remarked that the still missing compounds of this radical with sulphur and selenium would doubtlessly be found, and in reality they were discovered a few years afterwards.

This idea attracted some attention. It was adopted by Liebig, who gave the name of ethyle to the radical, which has been retained, though at first it was disputed by Dumas. The interchange of opinion which took place between these two chemists upon this subject soon induced Dumas to coincide with the

view adopted by Liebig, that the organic bodies containing oxygen were oxides of compound radicals. Their common opinion upon this subject was presented to the French Academy, Oct. 23, 1837, in a note by Dumas, in the names of both, 'Upon the actual state of Organic Chemistry.'

In that note Dumas proposes the question, How can we, from the known laws of inorganic chemistry, infer those applicable to organic bodies, which, though differently constituted, nearly all consist of carbon, hydrogen and oxygen, with the addition sometimes of nitrogen.

To preserve the vividness of his description, I will give a literal translation of his answer.

"This presents a great and beautiful problem to natural philosophy, a problem, the solution of which may well give rise to the highest degree of emulation amongst chemists, for, when once solved, the grandest triumphs are secured to science. The mysteries both of vegetable and animal life would be unveiled before our eyes, the key would be given to all the wonderfully rapid, often momentary modifications which take place in animals and plants; and still further, we might possibly discover the way to imitate these in our laboratories.

"And now, we fear not to announce it, nor is it on our part a hasty conclusion, this great and beautiful problem is *already* solved. We have now only to make from it all the deductions of which it is capable.

"With three or four elements Nature produces, in a manner as simple as it is productive, quite as various and perhaps more numerous compounds than occur in the whole of inorganic chemistry: from simple elements she produces compounds having all the properties of elements. It is our firm conviction, that in this the whole mystery of organic nature consists.

"Organic chemistry therefore embraces a number of peculiar elements, some of which play the part of oxygen or chlorine, others on the contrary correspond to the metals. Cyanogen, amidogen, benzoyle, the radicals of ammonia, of the fatty acids, of alcohol and similar bodies, are the elements with which organic chemistry works, and not with the simple elements carbon, hydrogen, nitrogen and oxygen, which only show themselves as such, when every trace of their organic origin has disappeared.

"In our opinion organic chemistry includes all bodies which

spring from the reciprocal union of simple elements, and organic chemistry must likewise embrace all such substances as are formed from compounds possessing the properties of simple elements.

"In mineral chemistry the radicals are simple, in organic they are compound—this is the whole difference. The laws upon which combination is based are in both the same.

"According to our view, organic chemistry presents us with radicals, which play the part of metals, and with others which play the part of oxygen, sulphur, chlorine, &c. These radicals combine with each other or with simple elements in accordance with the most simple laws of inorganic chemistry, and thus give rise to all organic compounds."

Amongst the details Dumas commits a palpable historical error when he affirms, that he and Liebig have been employed every day during the last ten years in endeavouring to discover and study these radicals.

Since that period I am not aware that Dumas has made any application of these views; Liebig however has retained them, and his 'Organic Chemistry' begins with the words, "Organic chemistry is the chemistry of compound radicals."

Both these chemists undertook an experiment, each after his own manner, and at the same time that the declaration of the above views was made, for the purpose of explaining theoretically the loss of water which anhydrous double salts of oxide of antimony and other bases experience when heated to 200° C.; both the explanations however which they have advanced appear to prove, that neither of them had given a thought to the theorems just mentioned, which both had so warmly advocated. Some time before he made the statement concerning organic radicals, Dumas began a closer examination of the fact discovered by Gay-Lussac, that wax exposed to dry chlorine gas gradually converted it into hydrochloric acid gas, without effecting any change of volume; from which it follows, that wax parts with its hydrogen and absorbs chlorine in such proportions, that both in the gaseous form occupy the same volume. Dumas felt the great importance which this fact must have upon the doctrine of organic composition, and commenced an investigation of the laws. He showed at the same time that the greater number of organic substances, when they are treated with chlorine or bromine, exchange hydrogen for the salt radical, generally in equivalent proportions of the elements replacing each other.

This gave rise to a theoretical explanation of the phænomenon which he called the Theory of Substitutions; and as most frequently the elements are exchanged in equivalent quantities, he framed for it the name of Metalepsy. He showed that an organic body, in which one or several equivalents of hydrogen had been exchanged for an equal number of equivalents of chlorine or bromine, retained its original saturating power, as well as several of its chemical properties, and that in many cases it could be proved to possess the same crystalline form. From these facts he came to the conclusion, *that the salt radical plays the same part in the new compound as hydrogen played in the original one*; and having discovered and analysed chloracetic acid (chloroxalic acid), he considered this view so thoroughly established, as to build upon it an entirely new theory of organic composition. In the electro-chemical theory chlorine is one of the most highly electro-negative bodies, hydrogen, on the contrary, electro-positive; and as, according to the view which he had taken, one element could play the same part in a chemical combination as another, Dumas concluded that the electro-chemical views were not sufficiently well-founded to find application in the scientific theory; and with reference to this he settled, that the part which an element plays in organic composition, does not depend upon its original properties, but upon the position which it occupies in the compound; thus then chlorine or any other element taking the position of the hydrogen can play exactly the same part as it does.

This induced him to give up the idea of the organic radicals, which however, having previously so strenuously advocated, he avoided openly to dispute; he compared them now no longer to the simple elements, but to carbonic oxide, sulphurous acid, deutoxide of nitrogen, and to the so-called hyponitric acid, NO^4. He now took quite another view of organic composition.

The elements combine in organic nature two or more with each other to form peculiar *types*, and in these types the atoms are arranged, for each particular type, in a fixed, and for those bodies belonging to the same type, in a similar manner; the characters of the compound depend upon the arrangement amongst the compound atoms, so that it becomes quite immaterial what element it is that occupies a certain position in the compound. In this manner the possibility of substitution is extended to other bodies besides hydrogen and the salt radicals. "The law of substitu-

tion," says Dumas, "presupposes that all the elements can supplant and replace each other, that simple can be substituted by compound bodies, so that not only oxygen, but also cyanogen, carbonic oxide, sulphurous acid, deutoxide of nitrogen, hyponitric acid, amidogen, or other compound bodies may occur as fundamental principles, take the place of hydrogen, and give rise to new substances."

Dumas has not succeeded in establishing clearly the fundamental idea of these types. But he assumes two kinds of them, *chemical types* and *mechanical* or *molecular* types.

I shall quote his own words:—

"1. Experience shows us that a body may lose one of its elements and take up in its place another, equivalent for equivalent. This is the general fact of the theory of substitutions.

"2. When this occurs, we may admit that its molecule always remains unchanged, forming a group, in which one of the elements simply occupies the space previously filled by another. This constitutes in my opinion a natural family.

"3. Amongst the bodies which are formed by substitution, the greater portion evidently retains the same chemical character as an acid or a base, and in the same degree as it did before the change by substitution. Such bodies form, in my opinion, a *chemical type*, or speaking in the terms of natural history, belong to the same genus."

The chemical types therefore represent, according to Dumas, a kind of natural historical genus of compounds, which all agree in possessing an equal number of equivalents united in the same manner, and have the same properties.

Here then are three generic characters. The *first*, or the number of equivalents, is quite easily and accurately determined by the atomic weight. The *second*, on the contrary, or the similar mode of union of the elements, is without any foundation, unless it can be discovered by the isomorphism of the compounds. Here then individual opinion has free scope to consider the simple atoms united together in the same manner or not. With regard to the *third*, Dumas appears originally to have considered the chemical characters of those bodies produced by substitution as so little changed (in proof of which he mentions acetic and chloracetic acid), that he may have meant merely a general accordance in the chemical characters; when however objections were raised to this, he replied, that bodies

must be understood to possess the same fundamental properties when they afforded the same products of decomposition, on exposure to the same decomposing agents, and that this was the case with bodies belonging to the same chemical type.

This he illustrated by the following example. If acetate of potash be mixed with hydrate of potash and subjected to *dry distillation,* carburetted hydrogen in minimo CH^2 is generated; and when chloroxalate of potash is *boiled with a strong solution of caustic potash,* perchloride of formyle is formed $C^2\,H\,Cl^3$. The mode of decomposition is however here quite different, for chloroxalate of potash distilled with hydrate of potash gives chloride of potassium, carbon, carbonate of potash and carburetted hydrogen, whilst acetate is decomposed into carbonic acid and carburetted hydrogen, and is not acted upon at all when boiled with caustic potash. Such however was the illustration given by Dumas of his view of fundamental properties. In order now to make carburetted hydrogen in minimo belong to the same chemical type as the perchloride of formyle, he assumed that the atom of the former consisted of $C^2\,H^4$, and that in the latter, $C^2\,H\,Cl^3$, the chlorine played the part of hydrogen; or that in the former the 3 atoms of hydrogen occupied a similar position to the 3 atoms of chlorine in the latter. It is hardly necessary to add that this view is entirely fanciful.

To give an idea of the views of atomic composition which arise from this theory, I will quote an example given by Dumas of the chemical type to which the oil of bitter almonds belongs, represented by the chemical formulæ required by this theory, in which the elements that play the same part are placed vertically the one above the other.

Oil of bitter almonds	$C^{14}\,H^6\,O^2$
Binacichloride (chloride) of benzoyle	$C^{14}\left\{\begin{matrix}H^5\\Cl\end{matrix}\right\}O^2$
Benzoic acid	$C^{14}\left\{\begin{matrix}H^5\\O\end{matrix}\right\}O^2$.
Binacisulphuret (sulphuret) of benzoyle	$C^{14}\left\{\begin{matrix}H^5\\S\end{matrix}\right\}O^2$
(Benzoate of amidogen) benzamide .	$C^{14}\left\{\begin{matrix}H^5\\NH^2\end{matrix}\right\}O^2$.

Amongst these very different compounds, the rational composition of which is expressed by the names here employed, it is not only presumed that chlorine, sulphur and oxygen play the same part, but that this is likewise the case with hydrogen;

they are therefore supposed to occupy the same position as one equivalent of hydrogen in the oil of bitter almonds, or in their prototype. The fifth example presents the most remarkable circumstance, that the same space which in oil of bitter almonds is occupied by 1 equivalent of hydrogen suffices not only for 2 equivalents of hydrogen, but in addition for 1 equivalent of nitrogen. The mechanical impossibility is no obstacle to this theory, and the supporters of metalepsy find no difficulty in replacing an equivalent of hydrogen by 4 atoms or equivalents of oxygen and 1 equivalent of nitrogen, or by 2 atoms of oxygen and 1 atom of sulphur.

It is consequently the most easily applicable of all theories, and we need not be surprised that at this moment it is most generally adopted for organic combinations; its author's well-earned celebrity in other ways is no doubt the chief reason for this. His treatises since the publication of this theory have mostly borne the title of 'Memoirs upon the Chemical Types' (*Mémoires sur les Types Chimiques*).

Many more objections could doubtless be raised against this theory, but those which we have noticed are sufficient to give an idea of the manner in which the metaleptic type-theory considers the rational composition of bodies in organic chemistry.

Simultaneously with Dumas, Laurent worked out the same theoretical view, and varied it in an endless manner. The extraordinary number of new compounds which he had the good fortune to discover during his really excellent researches, offered him abundant material to test his views upon, and as these researches were all undertaken for that object, his nomenclature has been framed entirely to suit it; thus he has almost forced chemists to accept his view of the mode of combination, and although during his further progress he has sometimes been obliged to alter his mode of conception, he has nevertheless endeavoured to change the views upon inorganic composition to suit his own upon organic. The fundamental idea upon which his opinions are based is however quite the same as that of Dumas, and consists in types and metalepsy.

The same chemical theme has likewise been varied by Gerhardt in a work upon organic chemistry, in which he allows no predecessor to outdo him in setting up fanciful explanations of the rational composition of bodies.

Persoz starts with the fundamental position, that such bodies

as consist of carbon, hydrogen and oxygen, should properly be considered as carburetted hydrogen, in which the equivalents of hydrogen are metaleptically replaced by an equal number of atoms of carbonic oxide, and that such a compound can then combine with carbonic acid. This is evidently the doctrine of the union of binary compounds, corresponding to the theory of substitution. Thus, for instance, alcohol consists empirically of $C^4 H^6 O^2$; according to Persoz, its rational formula is $=C^2\left\{\begin{matrix} H^6 \\ C^2 O^2 \end{matrix}\right\}$, *i. e.* in the formula $C^2 H^8$, 2 equivalents of hydrogen are exchanged for 2 equivalents of carbonic oxide. Acetic acid, on the contrary, the empirical formula of which is $=C^4 H^3 O^3$, takes its origin from $C^2 H^4$, in which 1 equivalent of hydrogen is exchanged for one of carbonic oxide, therefore $C^2\left\{\begin{matrix} H^3 \\ CO \end{matrix}\right\}$; and this body is then combined with 1 atom of carbonic acid $=C^2\left\{\begin{matrix} H^3 \\ CO \end{matrix}\right\} + \overline{CO^2}$.

Löwig takes a view of organic composition, in which certain fundamental compounds of carbon or water, or both, with oxygen, can unite with carbonic oxide or with carbonic acid, or with both at the same time. Thus, for instance, the rational composition of formic acid according to him is $=CHO+CO^2$, that of tartrylic acid $2CHO + CO + CO^2$, that of citric acid $C^2 H^2 O + CO + CO^2$, and that of malic acid isomeric with the last $C^2 H^2 + 2CO^2$.

Graham assumes that the simple atoms of every fundamental principle combine with each other according to certain types consisting of a definite number of atoms in a fixed and unchangeable order. When fundamental principles unite with each other, then the atoms are exchanged from the types by a sort of double decomposition, and when organic compounds are produced, carbon atoms are exchanged from the carbon type for hydrogen, nitrogen or oxygen atoms from their types, the places of these latter being filled by carbon atoms.

In this manner it is clear that anybody who undertakes to explain the rational composition of organic compounds and does not feel satisfied with what his predecessors have done, may fabricate or invent a new view of his own; nor is there any reason why this should have a limit, until some rule is sought for to guide us in the mode of proceeding which ought here to be followed.

I have already stated that such a rule already exists in the laws for the combinations of elements in inorganic nature. But it frequently happens, that even with the aid of the best guide, we are unable to obtain clear ideas. We must then be satisfied with the empirical composition, and defer establishing the rational, until our knowledge is sufficiently ripe to enable us to do so. When that is the case all will immediately admit and acknowledge its correctness. To increase, in the mean time, the number of imaginative theories is only to retard instead of advance the progress of science.

Which views of the rational composition of organic bodies can be considered as corresponding with the laws of combination observed in inorganic nature? That is the question which I shall now endeavour to answer.

The idea of compound radicals and of their union with oxygen, sulphur, salt radicals, &c., is, as I have previously shown, the best guide for our judgement which we can take from inorganic nature. It is not my intention to develope this idea here. That has already long been done, and I refer for further particulars to the fifth German edition of my 'Manual of Chemistry,' vol. i. S. 672.

But this idea, presupposing even that it is correct, as some experiments tried for the purpose seem to prove, instead of unveiling to our view all the mysteries of organic nature, as Dumas conjectured, rather discovers to us nothing at all concerning them. The number of compound radicals which we have as yet been able to establish with any degree of certainty is also very small.

If in every compound of carbon and hydrogen, or of carbon, nitrogen and hydrogen with oxygen, we were to consider all that is not oxygen as a given radical, we should be led into quite as erroneous an opinion, as when, in sulphate of oxide of formyle (Melsen's acide sulfacétique), we consider all that which is not oxygen as the radical of the acid; for the sulphuric acid contained in it, is united in quite a peculiar manner, or, as we express it, is conjoined with oxide of formyle, which accompanies the acid in all its combinations. In the edition of my 'Manual,' quoted above at page 459, vol. i., I have given the theoretical views concerning this class of compounds. They occur generally, and we have always reason to expect them, whenever the number of oxygen atoms in a compound atom is greater than 7,

although it does not follow that the conjugate union may not obtain when the oxygen atoms are in smaller number. As long as one of the bodies constituting a conjugate compound is an inorganic oxide, there is no difficulty in recognising the conjugate compound, or in ascertaining the composition of the conjunct. But when both the chemically active oxide and the other body constituting the conjunct are of organic composition, and contain the same elements, analysis then gives us not the slightest idea of the mode of combination, and its nature must be ascertained by some other means. Such means are however very seldom to be met with, and have only been applicable in a very few cases; we, however, possess sufficient to show that such a mode of combination exists.

When we turn our attention to the great number of conjugate compounds into which sulphuric acid enters, and which are already known, and when we learn that the number of organic bodies which do not produce such compounds with sulphuric acid is very limited; when we find that nitric acid, phosphoric acid, and even the chlorine acids, enter into the composition of conjugate compounds, it then appears that this mode of combination, although but quite recently properly understood, is nevertheless one of general occurrence; and it appears to be much more generally made use of in the œconomy of organic nature than in inorganic chemistry, so that the greater number of organic bodies may consist of conjugate compounds, which we should never be able to discover by the separation of their individual components. We only obtain a knowledge of the conjugate compounds themselves, and must be satisfied to consider these as peculiar definitive bodies.

We have discovered in inorganic chemistry that the affinity between the chemically active oxide and its conjunct is very various; sometimes the compound is decomposed by the weakest agencies, at other times the affinity is so strong that it can only be dissolved by the destruction of one of the constituent bodies. The oxygen of the chemically active oxide can be exchanged for sulphur, chlorine, &c., and the conjunct follows the radical from one combination to the other. The conjugate compound of subchloride of platinum with elayle can be decomposed by hydrate of potash, and the conjunct accompanies the platinum in the suboxide; it can be decomposed by zinc, and the platinum is eliminated still coupled with elayle. When such intimate con-

nexion exists between a compound radical and its conjunct, we can easily conceive how impossible it is to ascertain the relationship.

The grand difficulty in the application of the idea of compound radicals to the critical examination of the rational composition of organic compounds, consists in ascertaining whether the substance under examination is a single organic oxide or a conjugate compound. In the first case it is easy to obtain a notion of the radical, in the last it is impossible, for the active oxide has its radical, as has also the conjunct; and when the conjunct is a compound of two substances, each of these has likewise its radical. It is thus evident that the idea of compound radicals may be quite correct and yet not applicable under such circumstances, until we have obtained some knowledge of the composition both of the active oxide and of the conjunct. When this knowledge is unattainable, which it is in most cases, we must, as I have already noticed, consider the organic substance empirically as a single whole.

The number of compound radicals may perhaps not be very great; for it is possible that the endless multiplicity is produced by changes in the conjugate compounds. We have nearly 100 different acids into the composition of which sulphuric acid enters, only varying according to the different conjuncts which they contain.

I have already mentioned, that when the number of oxygen atoms in an organic atom exceeds seven, we have reason to presume that the compound belongs to the conjugate class of combinations, in which the conjoined amount of oxygen in the conjoined oxides together, may sometimes increase the atomic proportion of that element considerably. It occasionally happens that the amount of oxygen in these compounds may be lessened or increased. When this, however, only takes place with one of the combined oxides, the change never amounts to more than a small fraction of the whole quantity of oxygen contained in the combined oxides, and does not correspond with the multiple proportions which we are in the habit of meeting with in inorganic chemistry; but it is evident that it would correspond to these if we could calculate it for the oxide to which it appertains. Thus, for instance, proteine contains 10 atoms of oxygen, but the amount of oxygen can be raised by 2 or 3 atoms, to bin- and tritoxide of proteine with 12 and 13 atoms of oxygen. This un-

commonly small addition of oxygen points clearly to the existence of a conjugate compound, in which the increase of oxygen only pertains to the chemically active oxide.

In the case of oxamic acid, we have seen that to the bodies which may be conjuncts the amides likewise belong. Fehling's experiments upon succinic acid have shown that this acid gives with succinamide a similarly constituted conjugate succinic acid, and Laurent's researches prove the existence of similar conjugate acids with amidogen produced from tartaric, lactic, camphoric and phtalinic acids. From a single one, these examples have rapidly increased to a multitude. It is therefore evident that this mode of combination must be more general than we had previously reason to suppose. But this includes the doctrine of ternary radicals, into the composition of which nitrogen enters, in a manner which it is quite beyond our power to explain. As long as the amide is composed of an acid in a low grade of oxidation combined with NH^2, the kind of relationship is easily discovered, for acids and alkalies then convert the amide into ammonia or oxide of ammonium, by oxidizing, at the expense of water, the oxide with which it is combined. But when amides of a different kind, where such higher oxidation of the oxide cannot take place, and consequently the amidogen cannot be converted into ammonia, become conjuncts to organic oxides, nitrogenized or not nitrogenized, these cannot be discovered by the means just mentioned.

From all that has now been stated it is therefore evident, that although the view relating to compound radicals may be quite correct, there still remains a vast deal to be discovered before we can apply it in a satisfactory manner, and before we can with certainty distinguish between a combination of oxygen with a compound radical and a conjugate oxide.

Our rational view extends only to the fact, that we have succeeded in showing the existence of compound radicals, and that the combinations of these with oxygen, sulphur, salt radicals, &c. have a great and general tendency to the formation of conjugate compounds, in which one of the constituent bodies retains its chemical activity, whilst the other in most cases entirely loses it.

What relation do the phænomena of substitution bear to these views? This question arises spontaneously from what has just been stated.

It is evident that when a conjugate compound is acted upon

by chlorine or bromine, and an exchange takes place, this is not effected simultaneously in the conjunct and in the chemically active oxide. But in this manner quite a different view of the subject is obtained than that arising from the metaleptic theory. It cannot be considered merely as a supposition, when we assume that the conjunct is the first to be changed by the action of the salt radical, for I shall prove by striking examples that a conjunct can be thus changed by a salt radical without ceasing on that account to be still a conjunct to the chemically active oxide, which, if it happen to be an acid, retains its acid properties and forms salts, the characters of which are more or less changed, according to the changed constitution of the conjunct. This it was that gave rise to the fiction of chemical types. It however does not prevent the chemically active oxide from being eventually changed by the action of chlorine; but then quite another kind of compound is produced, in which the properties of the chemically active oxide are no longer to be found.

These substitutions have never been theoretically handled but by supporters of the metaleptic theory, and it must be admitted that almost every one who has made an attempt to investigate the subject has soon become a proselyte to that theoretical view. It will not be out of place here to examine these phænomena from another point of view, and with this motive I shall bring forward a few examples.

1. When oil of bitter almonds, or binoxide of picramyle, $C^{14} H^6 + O^2$, is treated with chlorine, an equivalent of hydrogen is exchanged for an equivalent of chlorine. By this process a body is produced which on its first discovery received the name of chlorbenzoyle. According to the metaleptic theory, from what has been already stated, it would be considered as an unaltered type $= C^{14} \left\{ \begin{matrix} H^5 \\ Cl \end{matrix} \right\} O^2$, and the chlorine would play the same part and take the same position in it as the equivalent of hydrogen which has been eliminated. But when the body is now treated in alcohol with hydrate of potash, chloride of potassium and benzoate of potash are produced. This indicates quite another mode of combination: it contains, namely, the same compound of carbon and hydrogen, which is present in benzoic acid, united with 2 atoms of oxygen and 1 equivalent of chlorine. The counterpart to this may be observed in numerous cases with inorganic radicals, for instance, with sulphur, chromium, tung-

sten, and molybdenum. But the combinations of these consist of 2 atoms of anhydrous acid with 1 atom of perchloride; such should also be the case here, and chlorbenzoyle-binacichloride should be = $2C^{14}H^5O^2 + C^{14}H^5Cl^3$.

Here consequently no substitution has been effected, but out of 3 atoms of binoxide of picramyle 2 atoms of benzoic acid and 1 atom of perchloride of benzoyle have been formed, which enter into combination with each other. The chlorine has destroyed the radical which was presented to it, and formed another, containing the same number of carbon atoms but an equivalent less of hydrogen. The relation therefore is clear and indisputable.

2. If chlorine is permitted to act upon a conjugate organic acid in which the conjunct is a carburetted hydrogen containing many atoms of each element, then the substitution must be exercised upon the hydrogen of the conjunct. What results here from the change cannot be positively proved, but the possible cases may be conceived without the necessity for assuming that any one in particular is actually produced.

a. A conjunct may consist of several atoms of the carburetted hydrogen: one of these alone, on substitution taking place, may part with its hydrogen for chlorine, by which means chloride of carbon and the remainder of the carburetted hydrogen united together to form a conjunct are left. Let the conjunct consist for instance of 3 atoms C^2H^3. Now if 1 atom C^2H^3 is converted by chlorine into C^2Cl^3, *i. e.* into sesquichloride of carbon, we obtain by substitution three acids, in which the acid body remains unchanged in each, but is united with three different conjuncts, namely, $C^2Cl^3 + 2C^2H^3$, $2C^2Cl^3 + C^2H^3$, and lastly $3C^2Cl^3$.

b. These successive exchanges of hydrogen for chlorine may, however, take place in another manner, with the formation of a differently constituted conjunct, of which mode of exchange I will in addition adduce the following proof. In the edition of my 'Manual' before noticed (vol. i. S. 709), I mentioned that acetic acid might possibly be a conjugate oxalic acid, in which the conjunct was C^2H^3. I do not think that it can at present be decided whether this is the case or not, but let us take it as an example. If acetic acid is = $C^2O^3 + C^2H^3$, and if an equivalent of hydrogen is exchanged in it for an equivalent of chlorine, we obtain C^2H^2Cl; or protochloride of elayle, which belongs to the class of bodies forming conjuncts to acids. If

another equivalent of hydrogen is exchanged for chlorine, we get $C^2 HCl^2$, bichloride of formyle, which is a conjunct to oxalic acid; after another exchange we obtain the perchloride of carbon, $C^2 C^3$, as conjunct to the acid, *i. e.* acetic acid has been converted into chloroxalic (acide chloracétique, Dumas). The experiments upon the action of chlorine on acetic acid have never been carried to their whole extent, it is therefore unknown whether these intermediate grades exist; should this however be the case, it is quite evident that acetic acid comprising $C^2 H^3$, must be a conjugate oxalic acid. If they do not exist, then the portion of acetic acid upon which the chlorine acts is transformed immediately into chloroxalic acid, which can be separated from the unaltered acetic acid. The chlorine in this case effects no substitution, but a decomposition of the acetic acid, and this would then be a reason for considering it an acid with an independent radical.

c. When the conjunct is an oxide with an independent radical, then, by the exchange of hydrogen for chlorine, an oxychloride of a radical with less hydrogen is produced, or, if all the hydrogen is exchanged, an oxychloride of carbon.

It is remarkable how a body which has once entered as a conjunct into combination can undergo one change after another in its composition and yet retain its properties as a conjunct. The compounds of indigo with sulphuric acid offer the most numerous examples. Indigo-blue as a conjunct to sulphuric acid undergoes the most numerous changes of composition by the action of salt radicals, nitric acid, alkalies, and reducing agencies, without giving up its connexion with sulphuric acid. I will now produce the positive proof of the changes which conjuncts undergo, deduced from inorganic chemistry, of which I have spoken before.

Kolbe, who recently published an examination of the changes produced in sulphuret of carbon by the action of chlorine, has shown, that the body produced by the action of chlorine or *aqua regia* upon sulphuret of carbon consists of perchloride of carbon and sulphurous acid, $C Cl^2 + SO^2$. This is a kind of conjugate combination of perchloride of carbon and sulphurous acid. When acted upon by caustic potash, a portion of the chlorine is exchanged for oxygen from the potash, and from 2 atoms $(CCl^2 + SO^2)$ we obtain 1 atom of chloride of potassium and 1 atom of a potash salt, the acid of which consists of 1 atom of

sesquichloride of carbon and 1 atom of dithyonic (hyposulphuric) acid = $C^2Cl^3 + S^2O^5$. This is a strong acid, which can be separated and crystallized; it may be called sesquichloride of carbon-dithyonic acid, and is evidently a conjugate dithyonic acid in which the conjunct is the same as in chloroxalic acid.

If metallic zinc is placed in a solution of this acid, it is dissolved without any evolution of gas, and two salts of zinc are obtained dissolved in the fluid. One atomic equivalent of the acid dissolves 2 atoms of zinc, and the solution contains 1 atom of protochloride of zinc and 1 atom of an oxide of zinc salt, the acid of which consists of $C^2HCl^2 + S^2O^5$. An equivalent of chlorine is taken up by the zinc, and the hydrogen which was eliminated on the formation of an atom of oxide of zinc to saturate the acid has taken its place in the conjunct, which now has been converted from sesquichloride of carbon into dichloride of formyle without leaving its position in the conjunct. This substitution, compared with the previous one, has taken place in an inverse order, and at the same time a compound radical has formed itself in the conjunct which was previously not present. When this or the first-named acid, no matter which, is dissolved in water, mixed with an equivalent of sulphuric acid, and zinc then added, the acid becomes saturated with zinc, without the evolution of hydrogen. According to the nature of the conjugate acid used, 3 or 4 equivalents of zinc are dissolved, and we obtain in solution 1 or 2 equivalents of protochloride of zinc, 1 equivalent of sulphate of zinc, and 1 equivalent of a new salt of zinc, in which only 1 equivalent of chlorine remains, the acid of which is $C^2H^2Cl + S^2O^5$, *i. e.* a conjugate acid composed of protochloride of elayle united to dithyonic acid. If more than 1 equivalent of sulphuric acid is used in the formation of this salt the protochloride of elayle is not decomposed, but on the solution of the zinc in the excess of acid hydrogen is given off.

What however the affinity exerted by an excess of sulphuric acid cannot overcome, is effected by an electrical current. Kolbe has shown that when the potash salt of either of these three conjugate dithyonic acids is exposed in a concentrated solution between amalgamated plates of zinc to the electric current produced by 2 or 3 pairs of Bunsen's carbo-zinc battery, by oxidizement of the zinc basic chloride of zinc is formed, and that no hydrogen is evolved, until the whole amount of chlorine in the acid has been exchanged for hydrogen. Thus we obtain a

fourth conjugate dithyonic acid $C^2H^3 + S^2O^5$, in which the conjunct has the composition of methyle. This is the same body which we suppositively adduced as a constituent of acetic acid, should this prove to be a conjugate oxalic acid.

Kolbe has further shown that chloroxalic acid can in the same manner be converted into acetic acid; and has also made mention of intermediate members of the series, the proof of the existence of which, once established with certainty, would be of the greatest importance to the science.

These simple experiments, in which the chemically active inorganic oxide is the same for all the acids, and consequently of such a nature, that its constituents do not interfere with the question concerning the changes effected by substitution in the conjunct, lead to the following simple deductions.

1. A conjunct can, notwithstanding its composition be completely changed, retain its position as a conjunct.

2. When the conjunct is a chloride of carbon, and the chlorine is partially exchanged for hydrogen, new radicals are produced consisting of carbon and hydrogen, the proto- and perchlorides of which still constitute the conjunct; and when the whole of the chlorine is exchanged, there results a carburetted hydrogen, which, as conjunct, takes the place of the chlorine compound. It follows from this, that when the exchange takes place in an inverse order, or when hydrogen is exchanged for chlorine, the process must be judged in the same manner.

3. A possibility is afforded by the agency of an electrical current of exchanging chlorine for hydrogen, and in this case carbon and hydrogen form together a radical, in which hydrogen can occupy the same position as chlorine did, but cannot therefore play the same part. This result of Kolbe's experiments completes the refutation of the metaleptic views and the fanciful theory of chemical types.

It is far from my intention to maintain that what has been here stated affords an explanation of all those cases in which hydrogen is empirically replaced by a salt radical. The internal process in these cases and the products may be of the most various nature. The fault which has always been committed, consists in the endeavour to give an explanation that should apply in every case. There are instances in which even hypochlorous and hypobromous acids appear to be constituents of the products.

I am not so sanguine as to hope that these views upon the difficulties attending the formation of a correct opinion of the rational composition of organic substances will be much listened to by the supporters of metalepsy. They embrace their theory with the full conviction of its infallibility, and little is to be effected against blind faith by argument and proof. But I nevertheless do not despair, that what has here been brought forward will find some consideration from the great number of chemists who have not previously had occasion to declare themselves in favour of any particular view of these questions.

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